

Chapter-17

Lesson-1

I – Acid-Base Solutions and the Common Ion Effect

- Adding a salt (an ionic solid) with a common ion to a weak acid solution or a weak base solution will change the equilibrium of the solution and thus will change the pH of the solution. This change is known as the common ion effect.
- The common ion effect is a part of Le Chatelier's principle.

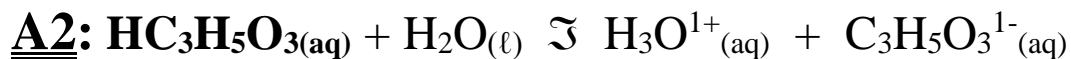
Q1: A 1.00 M solution of HNO_2 has a pH of 1.67 [$K_a = 4.5 \times 10^{-4}$]. Determine if the pH will increase, decrease, or remain the same when the following substances are added to the 1.00 M HNO_2 .

(i) $\text{HCl}_{(g)}$ (ii) $\text{KOH}_{(s)}$ (iii) $\text{KCl}_{(s)}$ (iv) $\text{NaNO}_{2(s)}$

A1: $\text{HNO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^{1+} + \text{NO}_2^{1-}$

- (i) Adding the strong acid, HCl , will increase the concentration of H_3O^{1+} forcing the equilibrium of the HNO_2 system to the left. Thus the pH will decrease.
- (ii) Adding the strong base, KOH , will increase the concentration of OH^{1-} in the solution. The OH^{1-} ions will react with and thus remove the H_3O^{1+} ions from the HNO_2 system forcing the equilibrium of the HNO_2 system to the right. Thus the pH will increase.
- (iii) Adding the neutral salt, KCl , will have no effect on the equilibrium of the HNO_2 system. Thus the pH will remain the same
- (iv) Adding the basic salt, NaNO_2 , will produce free NO_2^{1-} ions in the solution. This will force the equilibrium of the HNO_2 system to the left, thus the pH will increase.

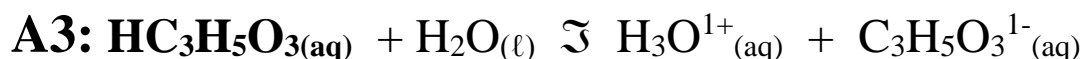
Q2: Lactic acid is $\text{HC}_3\text{H}_5\text{O}_3$ [$K_a = 1.4 \times 10^{-4}$]. Will the initial pH of 2.19 for a 0.300 M solution of lactic acid increase, decrease, or remain the same when solid $\text{NaC}_3\text{H}_5\text{O}_3(\text{s})$ is added?



Adding solid $\text{NaC}_3\text{H}_5\text{O}_3(\text{s})$ to the lactic acid solution will increase the concentration of $\text{C}_3\text{H}_5\text{O}_3^{1-}(\text{aq})$ and push equilibrium to the left. Thus the concentration of H_3O^{1+} will decrease and **pH will rise**.

Q3: Determine the new pH of a 1.00L solution of 0.300 M $\text{HC}_3\text{H}_5\text{O}_3$ [$K_a = 1.4 \times 10^{-4}$] after 20.0 g of $\text{NaC}_3\text{H}_5\text{O}_3$ is added.

Assume that the volume remains constant after adding the solid.



$$20.0 \text{ g NaC}_3\text{H}_5\text{O}_3 \times \frac{1 \text{ mol}}{112 \text{ g}} = 0.179 \text{ mol NaC}_3\text{H}_5\text{O}_3 \div 1.00 \text{ L} = \underline{\underline{0.179 \text{ M}}}$$

Assume that you initially have only $\text{HC}_3\text{H}_5\text{O}_3$ and $\text{NaC}_3\text{H}_5\text{O}_3$.

	$\text{HC}_3\text{H}_5\text{O}_3(\text{aq})$	$+$	$\text{H}_2\text{O}(\text{l})$	\rightleftharpoons	$\text{H}_3\text{O}^{1+}(\text{aq})$	$+$	$\text{C}_3\text{H}_5\text{O}_3^{1-}(\text{aq})$
I	0.300				0.000		0.179
C	- X				+ X		+ X
E	0.300-X				X		0.179+X

$$K_a = \frac{[\text{H}_3\text{O}^{1+}][\text{C}_3\text{H}_5\text{O}_3^{1-}]}{[\text{HC}_3\text{H}_5\text{O}_3]}$$

$$1.4 \times 10^{-4} = \frac{[\text{X}][0.179+X]}{[0.300-X]}$$

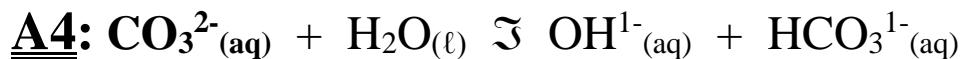
Since K_a is small, X might be small too in relation to both 0.300M and 0.179M

$$1.4 \times 10^{-4} = \frac{[\text{X}][0.179]}{[0.300]}$$

$$X = 0.00023 \text{ M H}^{1+} \rightarrow \boxed{\text{pH} = 3.64}$$

X is 0.077% ionization of 0.300 M $\text{HC}_3\text{H}_5\text{O}_3$ and 0.13% ionization of 0.179 M $\text{C}_3\text{H}_5\text{O}_3^{1-}$

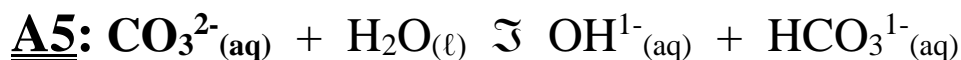
Q4: Washing soda is Na_2CO_3 [$K_b = 1.8 \times 10^{-4}$]. Will the initial pH of 11.63 for a 0.100 M solution of washing soda increase, decrease, or remain the same when some solid NaHCO_3 is added into it?



Adding solid NaHCO_3 to the Na_2CO_3 solution will increase the concentration of $\text{HCO}_3^-(\text{aq})$ and push equilibrium to the left. Thus the concentration of OH^- will decrease and **pH will fall**.

Q5: Determine the new pH of a 1.00L solution of 0.100 M Na_2CO_3 [$K_b = 1.8 \times 10^{-4}$] after 21.0 g of solid NaHCO_3 is added.

Assume that the volume remains constant after adding NaHCO_3 .



$$21.0\text{g NaHCO}_3 \times \frac{1 \text{ mol}}{84.0 \text{ g}} = 0.250 \text{ mol HCO}_3^- \div 1.00 \text{ L} = \underline{\underline{0.250 \text{ M}}}$$

Assume that you initially have only CO_3^{2-} and HCO_3^-

	CO_3^{2-}	+	H_2O	\rightleftharpoons	OH^-	+	HCO_3^-
I	0.100				0.000		0.250
C	- X				+ X		+ X
E	0.100-X				X		0.250+X

$$K_a = \frac{[\text{OH}^-][\text{HCO}_3^-]}{[\text{CO}_3^{2-}]}$$

$$1.8 \times 10^{-4} = \frac{[X][0.250+X]}{[0.100-X]}$$

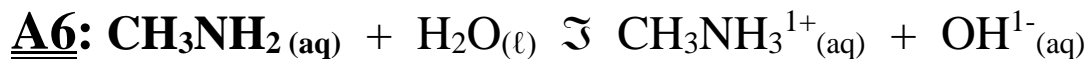
Since K_a is small, X might be small too in relation to both 0.100M and 0.250M

$$1.8 \times 10^{-4} = \frac{[X][0.250]}{[0.100]}$$

X is 0.072% ionization of 0.100 M CO_3^{2-} and 0.029% ionization of 0.250 M HCO_3^-

$$X = 0.000072 \text{ M OH}^- \rightarrow \text{pOH} = 4.14 \rightarrow \boxed{\text{pH} = 9.86}$$

Q6: Determine the pH of a 10.0 mL solution of 0.550 M CH_3NH_2 [$K_b = 4.4 \times 10^{-4}$] mixed with 15.0 mL of 0.450 M $\text{CH}_3\text{NH}_3\text{Cl}$. Assume that the liquid volumes are additive.



When mixing two solutions, it is necessary to recalculate the molarities because each solution **dilutes** the concentration of the other. Remember... $M_c V_c = M_d V_d$.

for CH_3NH_2 $M_c V_c = M_d V_d$

$$(0.450 \text{ M})(15.0 \text{ mL}) = (X)(25.0 \text{ mL})$$

$$X = \underline{\underline{0.220 \text{ M}}} \text{CH}_3\text{NH}_2$$

for $\text{CH}_3\text{NH}_3\text{Cl}$ $M_c V_c = M_d V_d$

$$(0.550 \text{ M})(10.0 \text{ mL}) = (X)(25.0 \text{ mL})$$

$$X = \underline{\underline{0.270 \text{ M}}} \text{CH}_3\text{NH}_3\text{Cl}$$

Assume that you initially have only CH_3NH_2 and $\text{CH}_3\text{NH}_3\text{Cl}$.

Rx	$\text{CH}_3\text{NH}_2(\text{aq})$	$+$	$\text{H}_2\text{O}(\ell)$	\rightleftharpoons	$\text{CH}_3\text{NH}_3^{1+}(\text{aq})$	$+$	$\text{OH}^{1-}(\text{aq})$
I	0.220				0.270		0.000
C	-X				+X		+X
E	0.220-X				0.270+X		X

$$K_b = \frac{[\text{CH}_3\text{NH}_3^{1+}][\text{OH}^{1-}]}{[\text{CH}_3\text{NH}_2]}$$

$$4.4 \times 10^{-4} = \frac{[0.270+X][X]}{[0.220-X]}$$

Since K_b is small, X might be small too in relation to both 0.270M and 0.220M

$$4.4 \times 10^{-4} = \frac{[0.270][X]}{[0.220]}$$

\nearrow X is 0.13% ionization of 0.270 M $\text{CH}_3\text{NH}_3^{1+}$ and 0.16% ionization of 0.220 M CH_3NH_2

$$X = 3.6 \times 10^{-4} \text{ M OH}^{1-} \rightarrow \text{pOH} = 3.44 \rightarrow \boxed{\text{pH} = 10.56}$$

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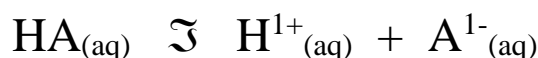
Lesson-2

II – Buffers

- A system whose pH changes only slightly when strong acid or strong base is added is called a **buffer system** or simply a **buffer**.
- A buffer ordinarily contains roughly equal amounts of a weak acid and its conjugate base (as a basic salt). $[HA] \approx [MA]$
- To create the buffer system: $HC_2H_3O_{2(aq)} \rightleftharpoons H^{1+}_{(aq)} + C_2H_3O_2^{1-}_{(aq)}$
dissolve equal amounts of $HC_2H_3O_2$ and $NaC_2H_3O_2$ in water.

A) $[H^+]$ in Solutions Made by Adding HA and A^{1-} to H_2O

- For the buffer system made by adding equal amounts of HA and NaA to water



$$K_a = \frac{[H^{1+}][A^{1-}]}{[HA]}$$

and

$$[H^{1+}] = \frac{K_a[HA]}{[A^{1-}]}$$

and

$$pH = pK_a + \log \frac{[A^{1-}]}{[HA]} \leftarrow \text{The Henderson-Hasselbalch Equation}$$

*Since HA is a weak acid assume that
[HA] added \approx [HA] at equilibrium.*

Q1: Calculate the $[H^+]$ and pH at equilibrium of a buffer prepared with 0.200 mol $HC_2H_3O_2$ ($K_a = 1.8 \times 10^{-5}$) and 0.200 mol $NaC_2H_3O_2$ in 1.00 L water.

A1: $pH = pK_a + \log ([A^{1-}]/[HA])$

$$pH = -\log (1.8 \times 10^{-5}) + \log([0.200]/[0.200]) \rightarrow \boxed{pH = 4.74}$$

$$\boxed{[H^+] = 1.8 \times 10^{-5} \text{ M}}$$

Note: $pH = pK_a$
when $[HA] = [A^{1-}]$

Q2: Calculate the pH at equilibrium of a buffer system prepared by adding 1.00 g NaHCO₃ and 1.00 g Na₂CO₃ to 1.00 L water.
(MM NaHCO₃ = 84.0 g/mol) (MM Na₂CO₃ = 106 g/mol) ($K_a \text{ HCO}_3^{1-} = 5.6 \times 10^{-11}$)

A2: NaHCO₃: $1.00 \text{ g} \times \frac{1 \text{ mole}}{84.0 \text{ g}} = 0.0119 \text{ mol} \div 1.00 \text{ L} = \underline{0.0119 \text{ M}}$

Na₂CO₃: $1.00 \text{ g} \times \frac{1 \text{ mole}}{106 \text{ g}} = 0.00943 \text{ mol} \div 1.00 \text{ L} = \underline{0.00943 \text{ M}}$

$$\text{pH} = \text{p}K_a + \log ([A^{1-}]/[HA])$$

$$\text{pH} = -\log (5.6 \times 10^{-11}) + \log ([0.00943]/[0.0119]) \rightarrow \boxed{\text{pH} = 10.15}$$

B) Choosing a Buffer System

- **NOTE:** If HA and A¹⁻ are present in roughly equal amounts, the pH of the buffer is roughly equal to the pK_a of the weak acid.
- To prepare a buffer of a particular pH, choose a system where the pK_a of the weak acid is roughly equal to the desired pH.
- A buffer has a useable **pH range** of about ± 1 pH unit of pK_a.
- The **buffer capacity** (the ability to resist change) is directly related to the initial concentrations of HA and A¹⁻.

Q3: Which of the following conjugate acid-base pairs will not function as a buffer? HF & F¹⁻, HClO & ClO¹⁻, HNO₃ & NO₃¹⁻

A3: HNO₃ & NO₃¹⁻ because HNO₃ is a strong acid.

Q4: What is the optimal pH buffered by a solution of HCHO₂ and NaCHO₂? (K_a of HCHO₂ = 1.8×10^{-4})

A4: pH = 3.74 because the pK_a of HCHO₂ = 3.74.

Q5: Which of the following 1.0 M conjugate acid-base pairs will best function as a pH 4.00 buffer? (consult the K_a values of the weak acids)

HF & NaF, HClO₂ & NaClO₂, or HC₆H₇O₆ & NaC₆H₇O₆

A5: HC₆H₇O₆ & NaC₆H₇O₆ because pK_a of HC₆H₇O₆ = 4.10

Q6: How would you prepare a 5.0 L buffer (pH = 4.25) with solid $\text{C}_6\text{H}_5\text{COOH}$ ($K_a = 6.3 \times 10^{-5}$) and a 0.050 M $\text{C}_6\text{H}_5\text{COONa}$ solution.

A6: $\text{pH} = \text{p}K_a + \log ([\text{A}^{1-}]/[\text{HA}])$

$$4.25 = -\log(6.3 \times 10^{-5}) + \log([0.050]/[\text{X}])$$

$$4.25 = 4.20 + (-1.30) - (\log \text{X})$$

$$4.25 = 2.90 - \log \text{X}$$

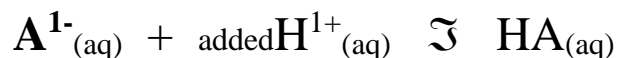
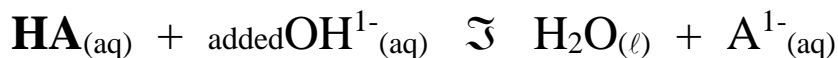
$$\log \text{X} = -1.35$$

$$\text{X} = \underline{0.045 \text{ M}} \times 5.0 \text{ L} \times \frac{122 \text{ g}}{1 \text{ mol}} = \boxed{27 \text{ g C}_6\text{H}_5\text{COOH}}$$

Dissolve 27 g $\text{C}_6\text{H}_5\text{COOH}$ in 4.0 L of 0.050 M $\text{C}_6\text{H}_5\text{COONa}$ solution and then bring the buffer solution up to 5.0 L with additional 0.050 M $\text{C}_6\text{H}_5\text{COONa}$ solution.

C) Effect of Stressing a Buffer System

- A buffer resists pH changes because it contains one species (HA) that reacts with OH^{1-} ions and another species (A^{1-}) that reacts with H^{1+} ions.



Thus, added H^{1+} or OH^{1-} is consumed and so pH remains stable.

Q7: Calculate the pH of a (0.200 mol $\text{HC}_2\text{H}_3\text{O}_2$ /0.200 mol $\text{C}_2\text{H}_3\text{O}_2^{1-}$) buffer ($K_a = 1.8 \times 10^{-5}$) after the addition of 0.020 mol NaOH.

A7: $\text{HC}_2\text{H}_3\text{O}_{2(\text{aq})} + \text{OH}^{1-}_{(\text{aq})} \rightleftharpoons \text{H}_2\text{O}_{(\ell)} + \text{C}_2\text{H}_3\text{O}_2^{1-}_{(\text{aq})}$

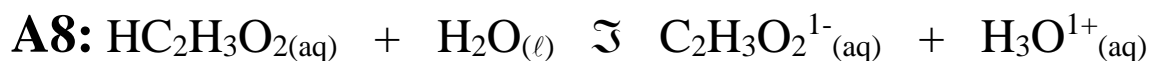
	$\text{HC}_2\text{H}_3\text{O}_2$ (mol)	$\text{C}_2\text{H}_3\text{O}_2^{1-}$ (mol)
Initial	0.200	0.200
Change	- 0.020	+ 0.020
Equilibrium	0.180	0.220

$$\text{pH} = \text{p}K_a + \log ([\text{C}_2\text{H}_3\text{O}_2^{1-}]/[\text{HC}_2\text{H}_3\text{O}_2])$$

$$\text{pH} = 4.74 + \log([0.220]/[0.180]) \rightarrow \boxed{\text{pH} = 4.83} \quad \Delta \text{pH of } 0.09$$

What happens when the concentration of the buffer system in the previous question is doubled and is then stressed in the same way?

Q8: Calculate the pH of a (0.400 mol HC₂H₃O₂/0.400 mol C₂H₃O₂¹⁻) buffer (K_a = 1.8×10⁻⁵) after the addition of 0.020 mol NaOH.



	HC ₂ H ₃ O ₂ (mol)	C ₂ H ₃ O ₂ ¹⁻ (mol)
Initial	0.400	0.400
Change	- 0.020	+ 0.020
Equilibrium	0.380	0.420

$$\text{pH} = \text{pK}_a + \log ([\text{C}_2\text{H}_3\text{O}_2^{1-}]/[\text{HC}_2\text{H}_3\text{O}_2])$$

$$\text{pH} = 4.74 + \log([0.420]/[0.380]) \rightarrow \boxed{\text{pH} = 4.78} \quad \Delta\text{pH of } 0.04$$

Notice that by increasing the concentration of the buffer system the buffer capacity is increased. The pH increased by only 0.04.

- Buffers can be made from weak bases and their conjugates.
- $\text{pOH} = \text{pK}_b + \log \frac{[\text{HB}^{1+}]}{[\text{B}]}$ ← Also the Henderson-Hasselbalch Equation

Q9: Calculate the final pH of the following 250.0 mL buffer system (1.0 M NH₃/1.0 M NH₄Cl) after the addition 100.0 mL of 0.10 M HNO₃. (K_b of NH₃ = 1.8×10⁻⁵)



$$250.0 \text{ mL} \rightarrow 0.2500 \text{ L} \times 1.0 \text{ M} = \mathbf{0.25 \text{ mol}} \text{ NH}_3 \text{ and NH}_4^{1+}$$

$$100.0 \text{ mL} \rightarrow 0.1000 \text{ L} \times 0.10 \text{ M} = \mathbf{0.010 \text{ mol}} \text{ HNO}_3 (\text{H}_3\text{O}^+)$$

	NH ₃ (mol)	NH ₄ ¹⁺ (mol)
Initial	0.25	0.25
Change	- 0.010	+ 0.010
Equilibrium	0.24	0.26

$$\text{pOH} = \text{pK}_b + \log ([\text{NH}_4^{1+}]/[\text{NH}_3])$$

$$\text{pOH} = 4.74 + \log([0.26]/[0.24]) \rightarrow \text{pOH} = 4.77 \rightarrow \boxed{\text{pH} = 9.23}$$

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Lesson-3

III – Solubility Equilibria of Ionic Solids

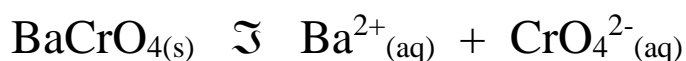
- When ionic solids dissolve in **pure** water, the extent to which solution occurs depends on a balance between three forces...
 - 1) the force of attraction between the water molecules and the ions of the ionic solid (i.e. **the ion-dipole forces**)
 - 2) the force of attraction between the cations and anions of the ionic solid (i.e. **the ionic bonds**).
 - 3) the force of attraction between the water molecules themselves (i.e. **the hydrogen bonds**).
- If the **ion-dipole forces** dominate, then we would expect the ionic solid to be very soluble in water. If the **ionic bonds** dominate, then we would expect the ionic solid to be very insoluble in water.
- By **learning the basic rules of solubility**, one can predict whether or not an ionic solid will **significantly** dissolve in **pure water**.

KCl is soluble in pure water. [34 g in 100 g H₂O at 25°C]

PbCl₂ is insoluble in pure water. [0.45 g in 100 g H₂O at 25°C]

AgCl is insoluble in pure water. [0.00019 g in 100 g H₂O at 25°C]

- Even the most insoluble ionic solutes dissolve in water - *to some extent* - before **saturation** occurs.
- All **saturated solutions** of ionic solids are equilibrium systems.
- The concentrations of the ions at equilibrium are governed by an equilibrium constant called the **solubility product constant** (**K_{sp}**).



$$K_{sp} = [\text{Ba}^{2+}][\text{CrO}_4^{2-}] = 2.10 \times 10^{-10}$$

A) Solubility of Ionic Solids in Pure Water

- Given a substance's K_{sp} , (**appendix D**) it is possible to calculate its solubility (**the maximum that will dissolve**) in pure water!

Q1: Calculate the solubility in water (**in mol/L**) of Li_2CO_3 at 25.0°C .
 $[K_{sp} = 1.70 \times 10^{-2}]$ [Solubility is the maximum that will dissolve.]

A1: $\text{Li}_2\text{CO}_{3(s)} \rightleftharpoons 2 \text{Li}^{1+}_{(aq)} + \text{CO}_3^{2-}_{(aq)}$ let **X** = the maximum that dissolves

	$\text{Li}_2\text{CO}_{3(s)}$	\rightleftharpoons	$2 \text{Li}^{1+}_{(aq)}$	$+$	$\text{CO}_3^{2-}_{(aq)}$
I	X		0.000		0.000
C	-X		+2X		+X
E	0		2X		X

$$K_{sp} = [\text{Li}^{1+}]^2[\text{CO}_3^{2-}]$$

$$1.70 \times 10^{-2} = [2X]^2[X] = 4X^3$$

$$X = 0.162 \text{ M} \rightarrow \text{the maximum that dissolves is } \boxed{0.162 \text{ M Li}_2\text{CO}_3}$$

Q2: Calculate the solubility in water (**in g/100 g H_2O**) of $\text{Ca}(\text{OH})_2$ at 25.0°C .
 $[K_{sp} = 6.5 \times 10^{-6}]$ (mole mass of $\text{Ca}(\text{OH})_2 = 74\text{g/mol}$)

A2: $\text{Ca}(\text{OH})_{2(s)} \rightleftharpoons \text{Ca}^{2+}_{(aq)} + 2 \text{OH}^{1-}_{(aq)}$ let **X** = the maximum that dissolves

	$\text{Ca}(\text{OH})_{2(s)}$	\rightleftharpoons	$\text{Ca}^{2+}_{(aq)}$	$+$	$2 \text{OH}^{1-}_{(aq)}$
I	X		0.000		0.000
C	-X		+X		+2X
E	0		X		2X

$$K_{sp} = [\text{Ca}^{2+}][\text{OH}^{1-}]^2$$

$$6.5 \times 10^{-6} = [X][2X]^2 = 4X^3$$

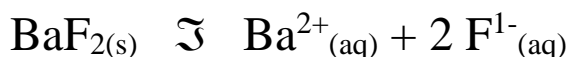
$$X = 0.012 \text{ M} \rightarrow \text{the maximum that dissolves is } 0.012 \text{ M Ca}(\text{OH})_2$$

$$0.012 \text{ mol/L} \times 74\text{g/mol} \times \underset{\text{an approximation}}{1\text{L}/1000 \text{ g}} \times 100\text{g} \approx \boxed{0.089 \text{ g}/100\text{gH}_2\text{O}}$$

- Given a substance's solubility (**the maximum that will dissolve**) in pure water, it is possible to calculate its K_{sp} !

Q3: A saturated solution of BaF_2 contains 1.38 g/L. Calculate the K_{sp} of BaF_2 . (*mole mass of $\text{BaF}_2 = 175\text{g/mol}$*)

A3: $1.38\text{ g/L} \times 1\text{mol}/175\text{ g} = 0.00789\text{ mol/L BaF}_2$



	$\text{BaF}_{2(s)}$	\rightleftharpoons	$\text{Ba}^{2+}_{(aq)}$	+	$2\text{F}^{-}_{(aq)}$
I	0.00789		0.000		0.000
C	-0.00789		+0.00789		+0.01578
E	0		0.00789		0.01578

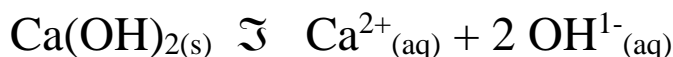
$$K_{sp} = [\text{Ba}^{2+}][\text{F}^{-}]^2$$

$$K_{sp} = [0.00789][0.0158]^2 \rightarrow \boxed{K_{sp} = 1.97 \times 10^{-6}}$$

Q4: If the solubility of solid $\text{Ca}(\text{OH})_2$ is 0.19g/100g H_2O at 0.0°C , then calculate its K_{sp} at 0.0°C . (*mole mass of $\text{Ca}(\text{OH})_2 = 74\text{g/mol}$*)

A4: $0.19\text{ g} \times 1\text{ mol}/74\text{g} = 0.0026\text{ mol Ca}(\text{OH})_2$ in 100 g H_2O

$$0.0026\text{ mol}/0.100\text{ L}_{(100\text{ g H}_2\text{O} \approx 0.100\text{ L solution})} = 0.026\text{ M Ca}(\text{OH})_2$$



	$\text{Ca}(\text{OH})_{2(s)}$	\rightleftharpoons	$\text{Ca}^{2+}_{(aq)}$	+	$2\text{OH}^{-}_{(aq)}$
I	0.026		0.000		0.000
C	-0.026		+0.026		+0.052
E	0		0.026		0.052

$$K_{sp} = [\text{Ca}^{2+}][\text{OH}^{-}]^2$$

$$K_{sp} = [0.026][0.052]^2 \rightarrow \boxed{K_{sp} = 7.0 \times 10^{-5}} \leftarrow \text{it's more than in question \#2!}$$

- Given a substance's K_{sp} , it is possible to calculate the minimum volume of water necessary dissolve a given mass of substance!

Q5: How many milliliters of a saturated $PbCl_2$ solution will contain 1.4 g of $PbCl_2$? ($K_{sp} = 1.7 \times 10^{-5}$)

A5: If you can find the moles of $PbCl_2$ that will saturate 1.00 L of water, then you can find the grams of $PbCl_2$ that will saturate 1.0 L of water, and then you can find the volume of water that would be saturated by 1.4 g of $PbCl_2$!



	$PbCl_{2(s)} \rightleftharpoons$	$Pb^{2+}_{(aq)}$	$+ 2 Cl^{1-}_{(aq)}$
I	X	0.000	0.000
C	-X	+X	+2X
E	0	X	2X

$$K_{sp} = [Pb^{2+}][Cl^{1-}]^2$$

$$1.7 \times 10^{-5} = [X][2X]^2 = 4X^3$$

$$X = \underline{\underline{0.016 \text{ M } PbCl_2}}$$

Thus, 0.016 mole $PbCl_2$ will saturate 1.0 L of water

$$0.016 \text{ mol} \times \frac{278 \text{ g}}{1 \text{ mol}} = \underline{\underline{4.4 \text{ g } PbCl_2 \text{ will saturate 1.0 L of water}}}$$

Now set up a proportion

$$\frac{4.4 \text{ g } PbCl_2}{1.0 \text{ L } H_2O} = \frac{1.4 \text{ g } PbCl_2}{X \text{ L } H_2O}$$

$$X = 0.32 \text{ L } H_2O \rightarrow \boxed{\boxed{320 \text{ mL } H_2O}}$$

Q6: Calculate the solubility in water (**in mol/L**) of Ag_2SO_4 at 25.0°C .
 $[\text{K}_{\text{sp}} = 1.5 \times 10^{-5}]$ [Solubility is the maximum that will dissolve.]

A6: $\text{Ag}_2\text{SO}_{4(\text{s})} \rightleftharpoons 2 \text{Ag}^{1+}_{(\text{aq})} + \text{SO}_4^{2-}_{(\text{aq})}$ let **X** = the maximum that dissolves

	$\text{Ag}_2\text{SO}_{4(\text{s})}$	\rightleftharpoons	$2 \text{Ag}^{1+}_{(\text{aq})}$	$+$	$\text{SO}_4^{2-}_{(\text{aq})}$
I	X		0.000		0.000
C	-X		+2X		+X
E	0		2X		X

$$\text{K}_{\text{sp}} = [\text{Ag}^{1+}]^2[\text{SO}_4^{2-}]$$

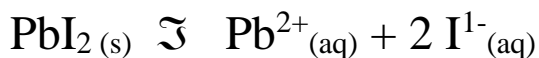
$$1.5 \times 10^{-5} = [2X]^2[X] = 4X^3$$

$$X = 0.016 \text{ M} \rightarrow \text{the maximum that dissolves is } \boxed{0.016 \text{ M Ag}_2\text{SO}_4}$$

Q7: If the solubility of solid PbI_2 is $0.069\text{g}/100\text{g H}_2\text{O}$ at 25°C , then calculate its K_{sp} at 25°C . (mole mass of $\text{PbI}_2 = 461\text{g/mol}$)

A7: $0.069 \text{ g} \times 1 \text{ mol}/461\text{g} = 1.5 \times 10^{-4} \text{ mol PbI}_2$

$$1.5 \times 10^{-4} \text{ mol}/0.100 \text{ L}_{(100 \text{ g H}_2\text{O} \approx 0.100 \text{ L solution})} = 1.5 \times 10^{-3} \text{ M PbI}_2$$



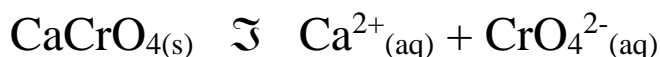
	$\text{PbI}_{2(\text{s})}$	\rightleftharpoons	$\text{Pb}^{2+}_{(\text{aq})}$	$+$	$2 \text{I}^{1-}_{(\text{aq})}$
I	1.5×10^{-3}		0.000		0.000
C	-1.5×10^{-3}		$+1.5 \times 10^{-3}$		$+3.0 \times 10^{-3}$
E	0		1.5×10^{-3}		3.0×10^{-3}

$$\text{K}_{\text{sp}} = [\text{Pb}^{2+}][\text{I}^{1-}]^2$$

$$\text{K}_{\text{sp}} = [1.5 \times 10^{-3}][3.0 \times 10^{-3}]^2 \rightarrow \boxed{\text{K}_{\text{sp}} = 1.4 \times 10^{-8}}$$

Q8: What volume in milliliters of a saturated CaCrO_4 solution will contain 1.0 g of CaCrO_4 at 25°C ? ($K_{\text{sp}} = 7.1 \times 10^{-4}$)

A8: If you can find the moles of CaCrO_4 that will saturate 1.00 L of water, then you can find the grams of CaCrO_4 that will saturate 1.0 L of water, and then you can find the volume of water that would be saturated by 1.0 g of CaCrO_4 !



	$\text{CaCrO}_{4(s)} \rightleftharpoons$	$\text{Ca}^{2+}_{(aq)} +$	$\text{CrO}_4^{2-}_{(aq)}$
I	X	0.000	0.000
C	-X	+X	+2
E	0	X	2

$$K_{\text{sp}} = [\text{Ca}^{2+}][\text{CrO}_4^{2-}]$$

$$7.1 \times 10^{-4} = [\text{X}][\text{X}] = \text{X}^2$$

$$\text{X} = \underline{0.027 \text{ M CaCrO}_4}$$

Thus, 0.027 mole CaCrO_4 will saturate 1.0 L of water

$$0.027 \text{ mol} \times \frac{156 \text{ g}}{1 \text{ mol}} = \underline{4.2 \text{ g}} \text{ **CaCrO_4 will saturate 1.0 L of water**}$$

Now set up a proportion

$$\frac{4.2 \text{ g CaCrO}_4}{1.0 \text{ L H}_2\text{O}} = \frac{1.0 \text{ g CaCrO}_4}{\text{X L H}_2\text{O}}$$

$$\text{X} = 0.24 \text{ L H}_2\text{O} \rightarrow \boxed{240 \text{ mL H}_2\text{O}}$$

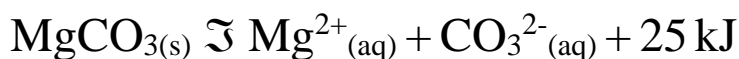
Chapter-17

Lesson-4

B) Solubility of Ionic Solids in Salt Solutions

- Compared with its solubility in pure water, an ionic solid is less soluble in an aqueous solution which already contains a common ion with the ionic solid. This is known as the **common ion effect**.
- The **common ion effect** is a part of Le Chatelier's principle.

Q1: Consider the equilibrium:



What effect does each of the following have on the position of the equilibrium? i) the addition of solid MgCl_2 . ii) an increase in the temperature of the solution. iii) the addition of solid NaCl . iv) an increase of pressure on the solution. v) the addition of solid NaOH (*be careful... a side reaction occurs*).

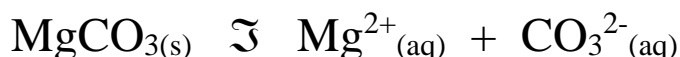
- A1:**
- i) With an increased concentration of aqueous Mg^{2+} ions, the equilibrium will shift to the left (common ion effect)
 - ii) The equilibrium will shift to the left since the forward reaction is exothermic and an increase in temperature will favor the endothermic (reverse) reaction.
 - iii) With no common ions, the equilibrium remains the same!
 - iv) Since there is no gaseous reactants or products in the system, then pressure will have no effect on the system.
 - v) Mg^{2+} ions are insoluble with OH^{1-} ions. Thus the precipitate $\text{Mg}(\text{OH})_2$ will form. This will cause a decrease in aqueous Mg^{2+} ions and thus the equilibrium will shift to the right.

Q2: The solubility of solid MgCO_3 in pure water is 0.012 g/L at 25°C. Would the solubility of solid MgCO_3 be greater, less, or the same in a 0.0025 M solution of MgCl_2 ?

A2: Since you are dissolving solid MgCO_3 in a solution that already contains aqueous magnesium ions, the solubility of solid MgCO_3 would be less.

Q3: Determine the solubility (in g/L) of solid MgCO_3 at 25°C in a 0.0025 M solution of MgCl_2 . (K_{sp} of $\text{MgCO}_3 = 2.0 \times 10^{-8}$)

A3: Since you are looking for MgCO_3 's solubility, then



is the equilibrium system.

☛ Remember, there already is 0.0025 M Mg^{2+} in the water to begin with (initially). **let X = the maximum that dissolves**

	$\text{MgCO}_{3(s)} \rightleftharpoons$	$\text{Mg}^{2+}_{(aq)} +$	$\text{CO}_3^{2-}_{(aq)}$
I	X	0.0025	0.000
C	-X	+X	+X
E	0	0.0025+X	X

$$K_{sp} = [\text{Mg}^{2+}][\text{CO}_3^{2-}]$$

$$2.0 \times 10^{-8} = [X][0.0025 + X] \rightarrow \text{since } K_{sp} \text{ is very small, then } +X \text{ can be ignored}$$

$$2.0 \times 10^{-8} \approx [X][0.0025]$$

$$X = \underline{8.0 \times 10^{-6} \text{ M}} \rightarrow [X \text{ is only } 0.32\% \text{ of } 0.0025 \text{ M}]$$

$$X = 8.0 \times 10^{-6} \frac{\text{mol}}{\text{L}} \times 84.3 \frac{\text{g}}{\text{mole}} = \boxed{6.7 \times 10^{-4} \text{ g/L MgCO}_3}$$

Q4: Determine the molar solubility of PbCl_2 ($K_{\text{sp}} = 1.7 \times 10^{-5}$) in 0.100 M CaCl_2 .

A4: $\text{PbCl}_{2(s)} \rightleftharpoons \text{Pb}^{2+}_{(aq)} + 2 \text{Cl}^{-}_{(aq)}$ let **X** = the maximum that dissolves

	$\text{PbCl}_{2(s)} \rightleftharpoons$	$\text{Pb}^{2+}_{(aq)} +$	$2 \text{Cl}^{-}_{(aq)}$
I	X	0.000	0.200
C	-X	+X	+2X
E	0	X	0.200+2X

0.100 M CaCl_2
will produce
0.200 M Cl^{-}

$$K_{\text{sp}} = [\text{Pb}^{2+}][\text{Cl}^{-}]^2$$

$$1.7 \times 10^{-5} = [\text{X}][0.200+2\text{X}]^2 \rightarrow \text{since } K_{\text{sp}} \text{ is small, then “+X” may be ignored.}$$

$$1.7 \times 10^{-5} \approx [\text{X}][0.200]^2$$

$$\boxed{\text{X} = 4.3 \times 10^{-4} \text{ M PbCl}_2} \quad (\text{X is only 0.22\% of 0.200 M})$$

Q5: Determine the molar solubility of Li_2CO_3 ($K_{\text{sp}} = 1.70 \times 10^{-2}$) in 0.100 M Na_2CO_3 .

A5: $\text{Li}_2\text{CO}_{3(s)} \rightleftharpoons 2 \text{Li}^{1+}_{(aq)} + \text{CO}_3^{2-}_{(aq)}$ let **X** = the maximum that dissolves

	$\text{Li}_2\text{CO}_{3(s)} \rightleftharpoons$	$2 \text{Li}^{1+}_{(aq)} +$	$\text{CO}_3^{2-}_{(aq)}$
I	X	0.000	0.100
C	-X	+2X	+X
E	0	2X	0.100+X

0.100 M Na_2CO_3
will produce
0.100 M CO_3^{2-}

$$K_{\text{sp}} = [\text{Li}^{1+}]^2[\text{CO}_3^{2-}]$$

$$1.70 \times 10^{-2} = [2\text{X}]^2[0.100+\text{X}] \rightarrow \text{since } K_{\text{sp}} \text{ is small, then “+X” may be ignored.}$$

$$1.70 \times 10^{-2} \approx [2\text{X}]^2[0.100]$$

$$\text{X} = 0.206 \text{ M} \rightarrow \text{which is } \underline{\underline{\text{HUGE}}} \text{ compared to 0.100 M !!!}$$

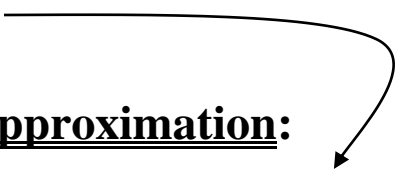
... So by using the method of successive approximations ...

take the **huge** answer for X (0.206 M) and insert it in for “+X”

$$1.70 \times 10^{-2} = [2X]^2[0.100 + X]$$


the first approximation:

$$1.70 \times 10^{-2} = [2X]^2[0.100 + \mathbf{0.206}]$$

$$X = 0.118 \text{ M}$$


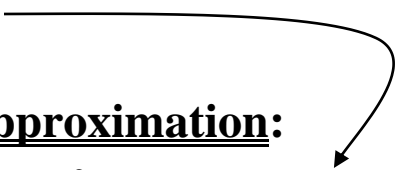
the second approximation:

$$1.70 \times 10^{-2} = [2X]^2[0.100 + \mathbf{0.118}]$$

$$X = 0.140 \text{ M}$$



the third approximation:

$$1.70 \times 10^{-2} = [2X]^2[0.100 + \mathbf{0.140}]$$

$$X = 0.133 \text{ M}$$


the fourth approximation:

$$1.70 \times 10^{-2} = [2X]^2[0.100 + \mathbf{0.133}]$$

$$X = 0.135 \text{ M}$$


the fifth approximation:

$$1.70 \times 10^{-2} = [2X]^2[0.100 + \mathbf{0.135}]$$

$$X = 0.134 \text{ M}$$


the sixth approximation:

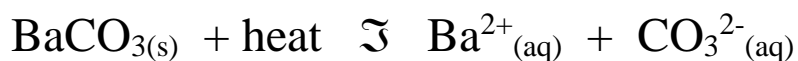
$$1.70 \times 10^{-2} = [2X]^2[0.100 + \mathbf{0.134}]$$

$$X = 0.135 \text{ M}$$

THUS the answer is... $X = 0.135 \text{ M Li}_2\text{CO}_3$

With the advent of powerful calculators, students no longer have to use this method of solving math problems.

Q6: Consider the equilibrium:



What effect does each of the following have on the position of the equilibrium? i) the addition of solid Na_2CO_3 . ii) an increase in the temperature of the solution. iii) the addition of solid NaCl . iv) an increase of pressure on the solution.

- A6:** i) With an increased concentration of aqueous CO_3^{2-} ions, the equilibrium will shift to the left (common ion effect)
- ii) The equilibrium will shift to the right since the forward reaction is endothermic and an increase in temperature will favor the endothermic (forward) reaction.
- iii) With no common ions, the equilibrium remains the same!
- iv) Since there is no gaseous reactants or products in the system, then pressure will have no effect on the system.

Q7: Determine the molar solubility of BaCO_3 ($K_{sp} = 5.0 \times 10^{-9}$) in pure water.



	$\text{BaCO}_{3(s)}$	\rightleftharpoons	$\text{Ba}^{2+}_{(aq)}$	+	$\text{CO}_3^{2-}_{(aq)}$
I	X		0.000		0.000
C	-X		+X		+X
E	0		X		X

$$K_{sp} = [\text{Ba}^{2+}][\text{CO}_3^{2-}]$$

$$5.0 \times 10^{-9} = [\text{X}][\text{X}]$$

$$5.0 \times 10^{-9} = [\text{X}]^2$$

$$\boxed{\text{X} = 7.1 \times 10^{-5} \text{ M BaCO}_3}$$

Q8: Determine the molar solubility of BaCO_3 ($K_{\text{sp}} = 5.0 \times 10^{-9}$) in a 0.100 M Na_2CO_3 solution (*not pure water*).

A8: $\text{BaCO}_3(\text{s}) \rightleftharpoons \text{Ba}^{2+}(\text{aq}) + \text{CO}_3^{2-}(\text{aq})$

	$\text{BaCO}_3(\text{s})$	\rightleftharpoons	$\text{Ba}^{2+}(\text{aq})$	+	$\text{CO}_3^{2-}(\text{aq})$
I	X		0.000		0.100
C	-X		+X		+X
E	0		X		0.100+X

0.100 M Na_2CO_3
will produce
0.100 M CO_3^{2-}

$$K_{\text{sp}} = [\text{Ba}^{2+}][\text{CO}_3^{2-}]$$

$$5.0 \times 10^{-9} = [\text{X}][0.100 + \text{X}] \rightarrow \text{since } K_{\text{sp}} \text{ is small, then "+X" may be ignored.}$$

$$5.0 \times 10^{-9} \approx [\text{X}][0.100]$$

$$\boxed{\text{X} = 5.0 \times 10^{-8} \text{ M BaCO}_3} \quad (\text{X is only } 0.000050\% \text{ of } 0.100 \text{ M})$$

Q9: Determine the solubility (in g/L) of solid BaF_2 at 25°C in a 0.075 M solution of BaCl_2 . (K_{sp} of $\text{BaF}_2 = 1.7 \times 10^{-6}$)

A9: $\text{BaF}_2(\text{s}) \rightleftharpoons \text{Ba}^{2+}(\text{aq}) + 2 \text{F}^{-}(\text{aq})$

	$\text{BaF}_2(\text{s})$	\rightleftharpoons	$\text{Ba}^{2+}(\text{aq})$	+	$2 \text{F}^{-}(\text{aq})$
I	X		0.075		0.000
C	-X		+X		+2X
E	0		0.075+X		2X

$$K_{\text{sp}} = [\text{Ba}^{2+}][\text{F}^{-}]^2$$

$$1.7 \times 10^{-6} = [0.075 + \text{X}][2\text{X}]^2 \rightarrow \text{since } K_{\text{sp}} \text{ is very small, then } +2\text{X} \text{ can be ignored}$$

$$1.7 \times 10^{-6} \approx [0.075][2\text{X}]^2$$

$$\text{X} = \underline{2.4 \times 10^{-3} \text{ M}} \rightarrow [\text{X is } 3.2\% \text{ of } 0.075 \text{ M}]$$

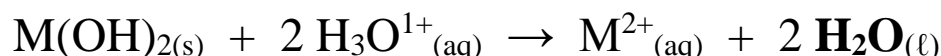
$$\text{X} = 2.4 \times 10^{-3} \frac{\text{mol}}{\text{L}} \times 175.3 \frac{\text{g}}{\text{mole}} = \boxed{0.42 \text{ g/L BaF}_2}$$

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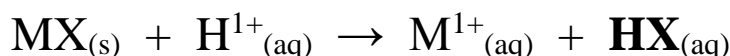
Lesson-5

C) Solubility of Ionic Solids and pH

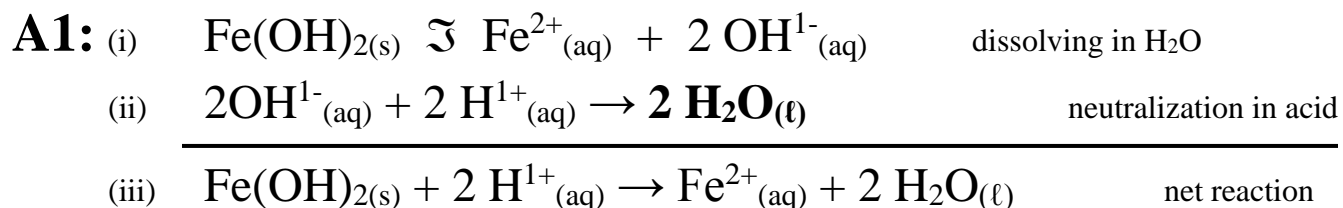
- Insoluble ionic compounds are often more soluble if the $\text{pH} \neq 7$.
- Insoluble hydroxides can readily dissolve in acidic solutions because water is formed which then pulls equilibrium to the right.



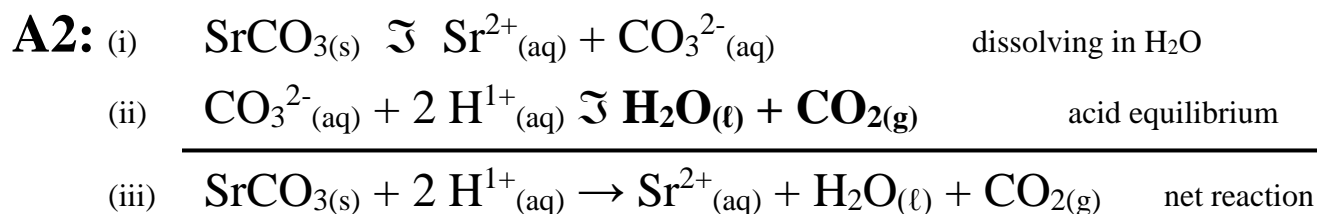
- Insoluble salts with anions of weak acids (ie: F^{1-} , S^{2-} , and CO_3^{2-}) are readily more soluble in acidic solutions because weak acid molecules are formed which then pulls equilibrium to the right.



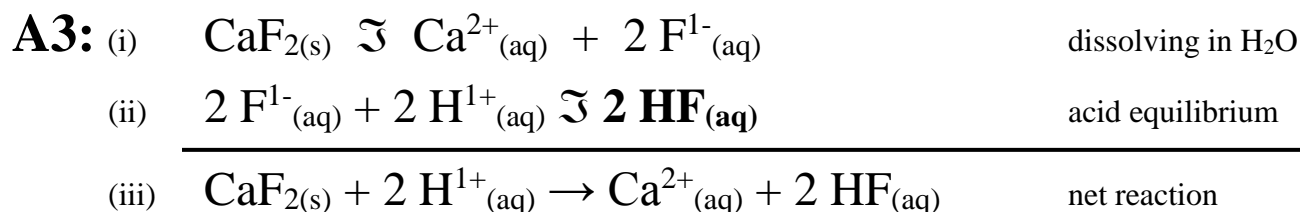
Q1: Write the dissolving equation of solid $\text{Fe}(\text{OH})_{2(\text{s})}$ in an acid solution.



Q2: Write the dissolving equation of solid $\text{SrCO}_{3(\text{s})}$ in an acid soln.



Q3: Write the dissolving equation of solid $\text{CaF}_{2(\text{s})}$ in an acid solution.



Q4: Calculate the molar solubility of $\text{Fe}(\text{OH})_2$ ($K_{\text{sp}} = 7.9 \times 10^{-16}$) in pure water.



	$\text{Fe}(\text{OH})_{2(s)} \rightleftharpoons$	$\text{Fe}^{2+}_{(aq)} +$	$2 \text{OH}^{-}_{(aq)}$
I	X	0.000	0.000
C	-X	+X	+2X
E	0	X	2X

$$K_{\text{sp}} = [\text{Fe}^{2+}][\text{OH}^{-}]^2$$

$$7.9 \times 10^{-16} = [\text{X}][2\text{X}]^2$$

$$[\text{X}] = 5.8 \times 10^{-6} \text{ M}$$

Thus only 5.8×10^{-6} moles $\text{Fe}(\text{OH})_{2(s)}$ will dissolve in 1.0 L of pure water

Q5: Calculate the molar solubility of $\text{Fe}(\text{OH})_2$ ($K_{\text{sp}} = 7.9 \times 10^{-16}$) in an acid solution that has been buffered at a pH of 6.20. *A buffered solution keeps the pH fairly constant even when acid or base is added.*



☛ **If pH = 6.20, then pOH = 7.80, and $[\text{OH}^{-}] = 1.6 \times 10^{-8} \text{ M}$**

	$\text{Fe}(\text{OH})_{2(s)} \rightleftharpoons$	$\text{Fe}^{2+}_{(aq)} +$	$2 \text{OH}^{-}_{(aq)}$
I	X	0.000	1.6×10^{-8}
C	-X	+X	+2X
E	0	X	$1.6 \times 10^{-8} + 2\text{X}$

A pH of 6.20 will produce $1.6 \times 10^{-8} \text{ M OH}^{-}$

$$K_{\text{sp}} = [\text{Fe}^{2+}][\text{OH}^{-}]^2$$

$$7.9 \times 10^{-16} = [\text{X}][1.6 \times 10^{-8} + 2\text{X}]^2$$

$$7.9 \times 10^{-16} = [\text{X}][1.6 \times 10^{-8}]^2$$

If the solution is buffered, then the “+2X” is negligible!

$$[\text{X}] = 3.1 \text{ M}$$

Thus 3.1 moles $\text{Fe}(\text{OH})_{2(s)}$ will dissolve in 1.0 L of the acid solution! This is a lot for a base that is insoluble in pure water!

- The solubility in solution of any insoluble hydroxide versus pH can be determined as shown by the problem below.

Q6: Determine the relationship between the solubility of $\text{Fe}(\text{OH})_2$ ($K_{\text{sp}} = 7.9 \times 10^{-16}$) in water and the pH of the water.



$$K_{\text{sp}} = [\text{Fe}^{2+}][\text{OH}^{-}]^2 = 7.9 \times 10^{-16}$$

$$\log [\text{Fe}^{2+}] + 2\log [\text{OH}^{-}] = -15.10$$

$$\log [\text{Fe}^{2+}] + 2(-\text{pOH}) = -15.10$$

$$-\log [\text{Fe}^{2+}] + 2(\text{pOH}) = 15.10$$

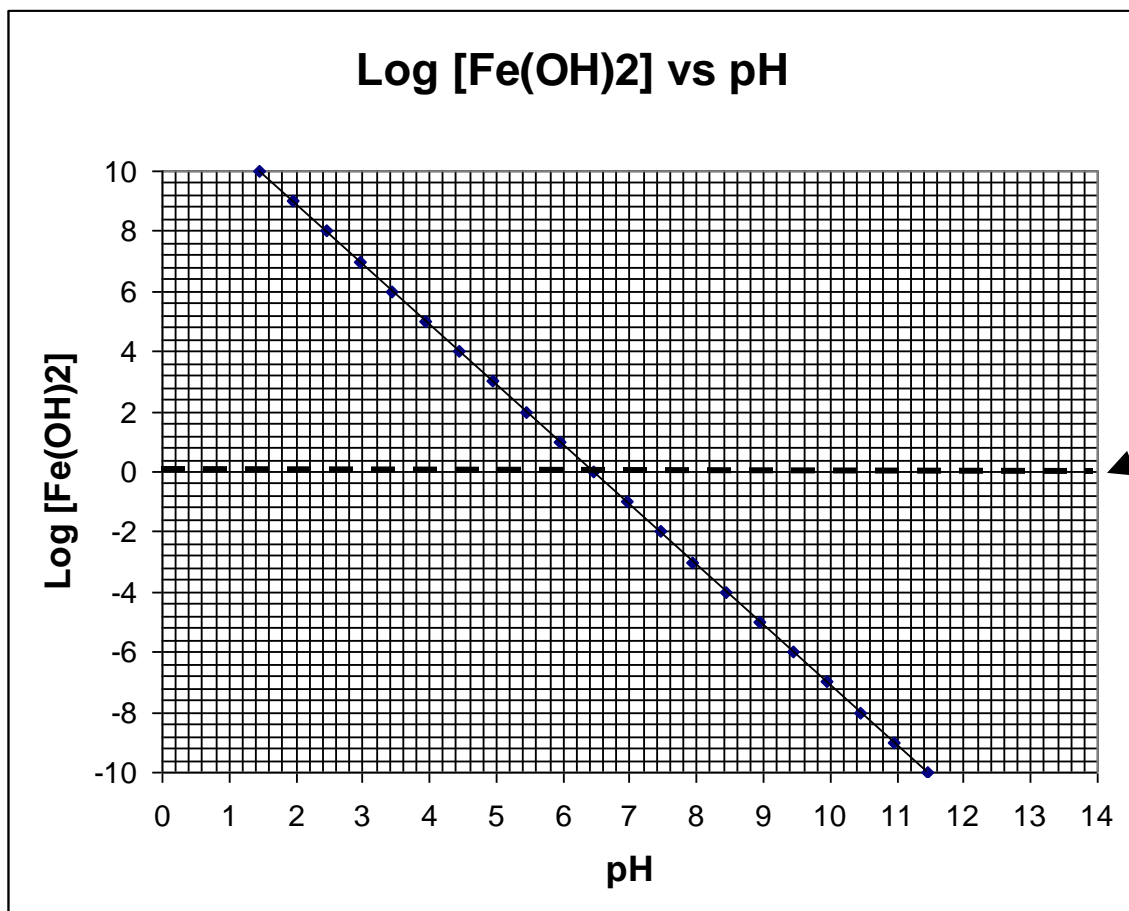
$$-\log [\text{Fe}^{2+}] + 2(14.00 - \text{pH}) = 15.10$$

$$-\log [\text{Fe}^{2+}] + 28.00 - 2\text{pH} = 15.10$$

$$2\text{pH} = 12.9 - \log [\text{Fe}^{2+}]$$

$$\text{pH} = 6.45 - \frac{1}{2} \log [\text{Fe}^{2+}]$$

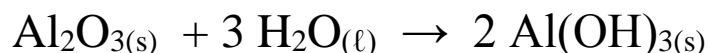
At a pH of 6.45, the solubility of $\text{Fe}(\text{OH})_2$ in solution is 1.0 M.



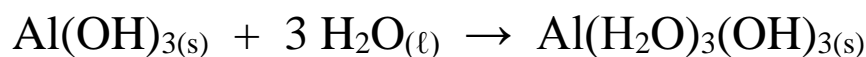
- Certain metallic oxides and metallic hydroxides are insoluble in pure water but are soluble in both acidic and basic solutions.
- These are called *amphoteric oxides and bases*.
- Oxides and hydroxide bases of Al^{3+} , Cr^{3+} , Zn^{2+} , and Sn^{2+} are amphoteric. Al_2O_3 & $\text{Al}(\text{OH})_3$ are the most common examples.

Example:

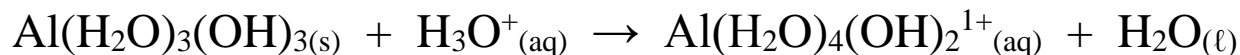
☞ In pure water, $\text{Al}_2\text{O}_{3(s)}$ forms insoluble $\text{Al}(\text{OH})_{3(s)}$



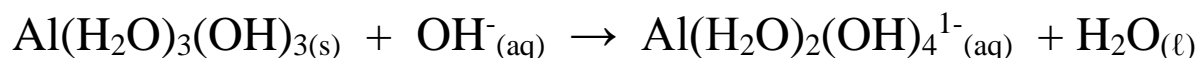
☞ In pure water, $\text{Al}(\text{OH})_{3(s)}$ forms insoluble $\text{Al}(\text{H}_2\text{O})_3(\text{OH})_{3(s)}$.



☞ In acid, $\text{Al}(\text{H}_2\text{O})_4(\text{OH})_2^{1+}_{(\text{aq})}$ forms which is soluble.

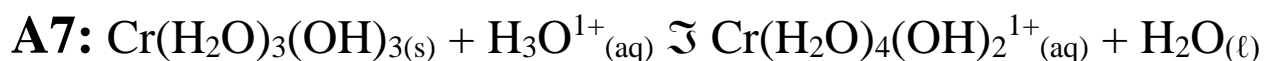


☞ In base, $\text{Al}(\text{H}_2\text{O})_2(\text{OH})_4^{1-}_{(\text{aq})}$ forms which is soluble.



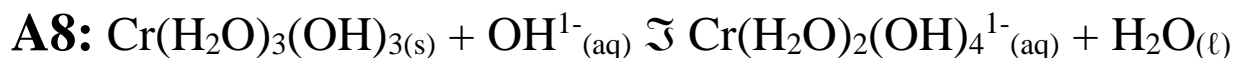
Q7: In water, insoluble $\text{Cr}(\text{OH})_{3(s)}$ exists as $\text{Cr}(\text{H}_2\text{O})_3(\text{OH})_{3(s)}$.

Write a reaction that shows $\text{Cr}(\text{OH})_{3(s)}$ dissolving in acid.

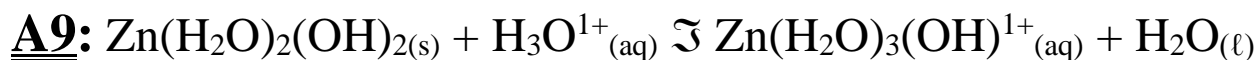


Q8: In water, insoluble $\text{Cr}(\text{OH})_{3(s)}$ exists as $\text{Cr}(\text{H}_2\text{O})_3(\text{OH})_{3(s)}$.

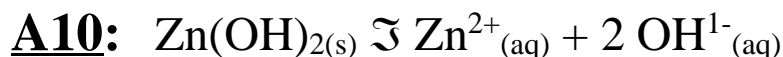
Write a reaction that shows $\text{Cr}(\text{OH})_{3(s)}$ dissolving in base.



Q9: In water, insoluble $\text{Zn(OH)}_{2(s)}$ exists as $\text{Zn(H}_2\text{O)}_2(\text{OH})_{2(s)}$.
Write a reaction that shows $\text{Zn(OH)}_{2(s)}$ dissolving in acid.



Q10: A saturated solution of Zn(OH)_2 [$K_{sp} = 2.0 \times 10^{-17}$] has a solubility in **pure water** of 1.7×10^{-5} g/100 g H_2O . This solution has a pH of 8.53. What would be the solubility of Zn(OH)_2 (in **g/100 g solution**) in an acid solution that is buffered at pH 6.00?



☛ If pH = 6.00, then pOH = 8.00, and $[\text{OH}^{1-}] = 1.0 \times 10^{-8}$ M

	$\text{Zn(OH)}_{2(s)} \rightleftharpoons$	$\text{Zn}^{2+}_{(aq)} +$	$2 \text{OH}^{1-}_{(aq)}$
I	X	0.000	1.0×10^{-8}
C	-X	+X	+2X
E	0	X	$1.0 \times 10^{-8} + 2X$

A pH of 6.00
will produce
 1.0×10^{-8} M OH^{1-}

$$K_{sp} = [\text{Zn}^{2+}][\text{OH}^{1-}]^2$$

$$2.0 \times 10^{-17} = [X][1.0 \times 10^{-8} + 2X]^2$$

$$2.0 \times 10^{-17} = [X][1.0 \times 10^{-8}]^2$$

$$[X] = 0.20 \text{ M}$$

If the solution is
buffered, then the
“+2X” is negligible!

Thus 0.20 moles $\text{Zn(OH)}_{2(s)}$ will dissolve in 1.0 L (≈ 1000 g) of the acid solution and in 100 g of acid solution, 0.020 moles of Zn(OH)_2 would dissolve.

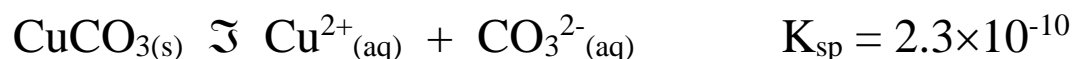
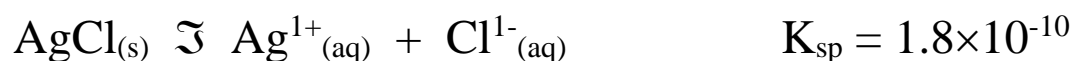
$$\frac{0.020 \text{ mol Zn(OH)}_2}{100 \text{ g acid solution}} \times \frac{99.4 \text{ g}}{1 \text{ mole}} = \boxed{\frac{2.0 \text{ g Zn(OH)}_2}{100 \text{ g acid solution}}}$$

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Lesson-6

D) Solubility of Ionic Solids that form Complex Ions

- Many ionic solids are insoluble in pure water.



- Certain Lewis bases are able to form stable complex ions with certain metallic cations (*the larger the K_f value – the more stable the complex ion*).



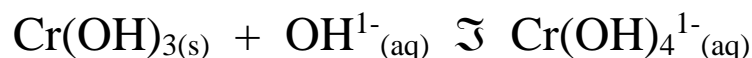
- Thus, the presence of certain Lewis bases will greatly increase the solubility of certain insoluble ionic compounds if a stable complex ion is able to form.



$$K_{eq} = K_{sp} \times K_f \quad \rightarrow \quad K_{eq} = 1.8 \times 10^{11}$$

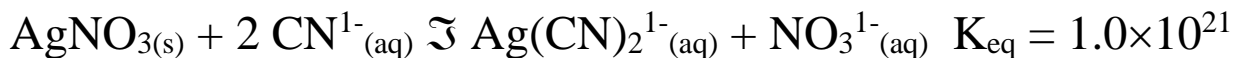
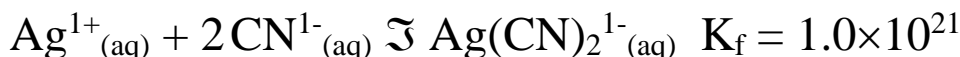
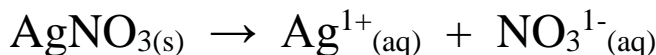


$$K_{eq} = K_{sp} \times K_f \quad \rightarrow \quad K_{eq} = 1200$$

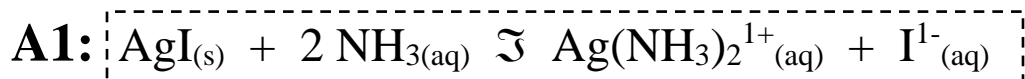


$$K_{eq} = K_{sp} \times K_f \quad \rightarrow \quad K_{eq} = 1.3$$

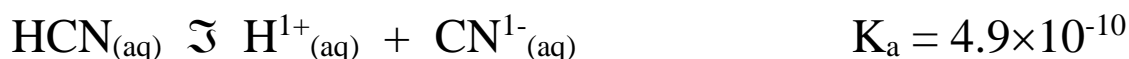
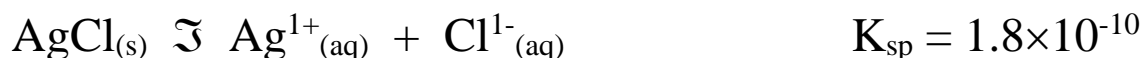
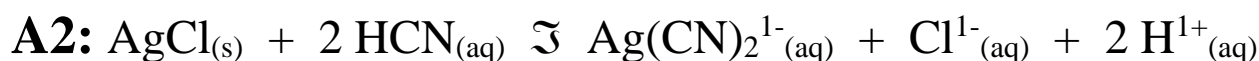
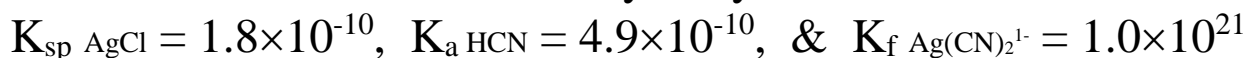
- The presence of certain Lewis bases will greatly decrease the presence of certain free aqueous metallic cations if a stable complex ion is able to form.

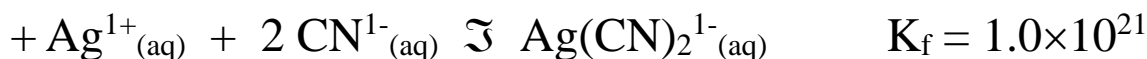
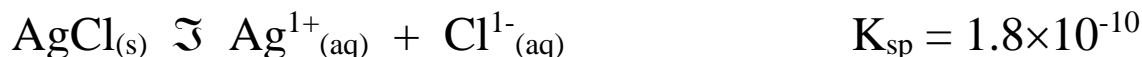


Q1: Write the equation for the dissolution of solid silver iodide in an aqueous solution of ammonia.



Q2: Calculate the equilibrium constant for the dissolution of solid silver chloride in a solution of hydrocyanic acid.





$$K_{eq} = K_{sp} \times K_a^2 \times K_f$$

$\boxed{K_{eq} = 4.3 \times 10^{-8}}$

Q3: To what final concentration of CN^{1-} must a solution contain in order to have just dissolved 0.070 mol of $\text{AgCl}_{(s)}$ in 1.0 L of solution? K_{sp} of $\text{AgCl} = 1.8 \times 10^{-10}$ & K_f of $\text{Ag}(\text{CN})_2^{1-} = 1.0 \times 10^{21}$



	$\text{AgCl}_{(s)}$	+	$2 \text{CN}^{1-}_{(aq)}$	\rightleftharpoons	$\text{Ag}(\text{CN})_2^{1-}_{(aq)}$	+	$\text{Cl}^{1-}_{(aq)}$
I	0.070 M		X+0.140		0.000		0.000
C	- 0.070 M		- 0.140		+ 0.070 M		+ 0.070 M
E	0.000		X		0.070 M		0.070 M

$$K_{eq} = \frac{[\text{Ag}(\text{CN})_2^{1-}][\text{Cl}^{1-}]}{[\text{CN}^{1-}]^2}$$

$$1.8 \times 10^{11} = \frac{[0.070 \text{ M}][0.070 \text{ M}]}{[\text{X}]^2}$$

$$\boxed{\text{X} = 1.6 \times 10^{-7} \text{ M CN}^{1-}}$$

Q4: Calculate the molar solubility of solid AgI in a 2.5 M solution of $\text{NH}_{3(aq)}$. K_{sp} of $\text{AgI} = 8.3 \times 10^{-17}$ & K_f of $\text{Ag}(\text{NH}_3)_2^{1+} = 1.7 \times 10^7$



	$\text{AgI}_{(s)}$	+	$2 \text{NH}_{3(aq)}$	\rightleftharpoons	$\text{Ag}(\text{NH}_3)_2^{1+}_{(aq)}$	+	$\text{I}^{1-}_{(aq)}$
I	X		2.5		0.0		0.0
C	- X		- 2X		+ X		+ X
E	0.0		2.5 - 2X		X		X

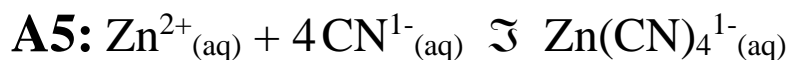
$$K_{eq} = \frac{[\text{Ag}(\text{NH}_3)_2^{1+}][\text{I}^{1-}]}{[\text{NH}_3]^2}$$

$$1.4 \times 10^{-9} = \frac{[\text{X}][\text{X}]}{[2.5 - 2\text{X}]^2}$$

$$\boxed{\text{X} = 9.4 \times 10^{-5} \text{ M AgI}}$$

Q5: When 0.82 g of ZnCl_2 is dissolved 255 mL of 0.150 M NaCN ,

what are the final concentrations of Zn^{2+} , CN^{1-} , $\text{Zn}(\text{CN})_4^{2-}$, Na^{1+} , and Cl^{1-} present in the solution? K_f of $\text{Zn}(\text{CN})_4^{2-} = 4.2 \times 10^{19}$



$$0.82 \text{ g} \times \frac{1 \text{ mole}}{136.3 \text{ g}} \times \frac{1}{0.255 \text{ L}} = 0.024 \text{ M ZnCl}_2$$

	$\text{Zn}^{2+}_{(\text{aq})}$	$+ 4\text{CN}^{1-}_{(\text{aq})}$	$\rightleftharpoons \text{Zn}(\text{CN})_4^{1-}_{(\text{aq})}$
I	0.024 M	0.150 M	0.000
C	- 0.024 M	- 0.096 M	+ 0.024 M
E	0.000	0.054	0.024 M

These final concentrations assume that the equilibrium “**went completely to the right**” and that **ALL** the Zn^{2+} ions are in the $\text{Zn}(\text{CN})_4^{1-}$. But there must be some free Zn^{2+} ions, so ...

...the equilibrium of the system shifts back slightly to the left!

	$\text{Zn}(\text{CN})_4^{1-}_{(\text{aq})}$	$\rightleftharpoons \text{Zn}^{2+}_{(\text{aq})} + 4\text{CN}^{1-}_{(\text{aq})}$
I	0.024 M	0.000
C	- X	+ X
E	0.024 - X	X

$$K_{\text{eq}} = \frac{[\text{Zn}^{2+}][\text{CN}^{1-}]^4}{[\text{Zn}(\text{CN})_4^{1-}]}$$

$$2.4 \times 10^{-20} = \frac{[\text{X}][0.054 + 4\text{X}]^4}{[0.024 - \text{X}]} \quad \text{Since } K_{\text{eq}} \text{ is small, } X \text{ might be small in relation to both } 0.054 \text{ and } 0.024$$

$$2.4 \times 10^{-20} = \frac{[\text{X}][0.054]^4}{[0.024]}$$

$$X = 6.8 \times 10^{-17} \text{ M Zn}^{2+}$$

Final Concentrations:

$$[\text{Zn}^{2+}] = 6.8 \times 10^{-17} \text{ M}$$

$$[\text{CN}^{1-}] = 0.054 \text{ M}$$

$$[\text{Zn}(\text{CN})_4^{2-}] = 0.024 \text{ M}$$

$$[\text{Na}^{1+}] = 0.150 \text{ M}$$

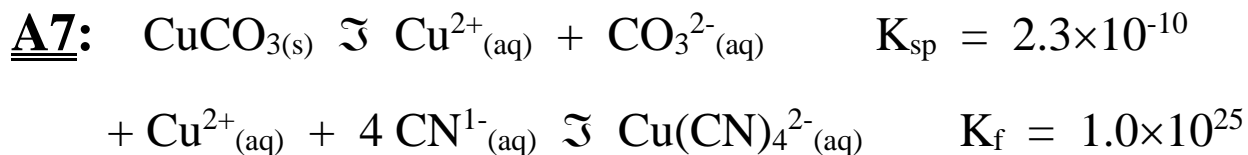
$$[\text{Cl}^{1-}] = 0.048 \text{ M}$$

Q6: Write the equation for the dissolution of solid copper (II) carbonate in a solution of cyanide. Each copper (II) ion complexes with four cyanide ions.



Q7: Calculate the equilibrium constant for the dissolution of solid copper (II) carbonate in an aqueous solution of sodium cyanide.

$$K_{sp} \text{ CuCO}_3 = 2.3 \times 10^{-10} \quad \& \quad K_f \text{ Cu}(\text{CN})_4^{2-} = 1.0 \times 10^{25}$$



$$K_{eq} = K_{sp} \times K_f$$

$K_{eq} = 2.3 \times 10^{15}$

Q8: To what final concentration of CN^{1-} must a solution contain in order to have just dissolved 10.0 g (0.0809 mol) of $\text{CuCO}_{3(s)}$ in 1.0 L of solution? $K_{sp} \text{ CuCO}_3 = 2.3 \times 10^{-10} \quad \& \quad K_f \text{ Cu}(\text{CN})_4^{2-} = 1.0 \times 10^{25}$



	$\text{CuCO}_{3(s)} + 4 \text{CN}^{1-}_{(aq)} \rightleftharpoons \text{Cu}(\text{CN})_4^{2-}_{(aq)} + \text{CO}_3^{2-}_{(aq)}$			
I	0.0809 M	X + 0.3236 M	0.0000 M	0.0000 M
C	-0.0809 M	-0.3236 M	+0.0809 M	+0.0809 M
E	0.0000 M	X	0.0809 M	0.0809 M

$$K_{eq} = \frac{[\text{Cu}(\text{CN})_4^{2-}][\text{CO}_3^{2-}]}{[\text{CN}^{1-}]^4}$$

$$2.3 \times 10^{15} = \frac{[0.0809 \text{ M}][0.0809 \text{ M}]}{[\text{X}]^4}$$

$\text{X} = 4.1 \times 10^{-5} \text{ M CN}^{1-}$

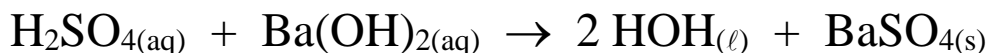
Chapter-17

Lesson-7

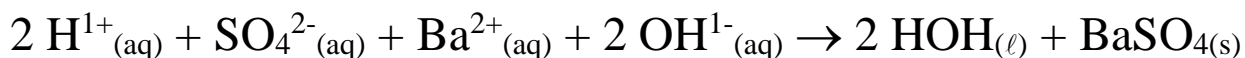
IV – Precipitation Reactions

- When solutions of two different **electrolytes** (acid, base, or salt) are mixed, an insoluble solid sometimes forms! This solid is called a **precipitate**.
- The chemical reaction by which a precipitate is formed is called **precipitation**.

- A precipitation reaction can be written in its molecular form.



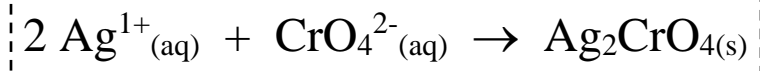
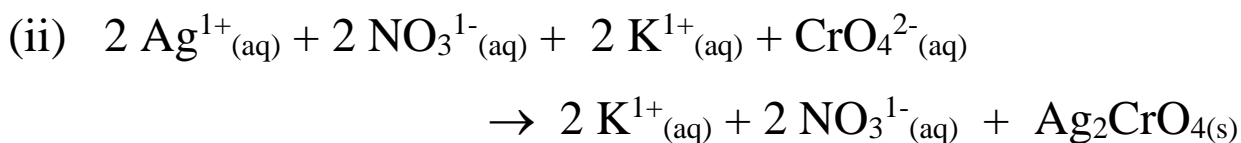
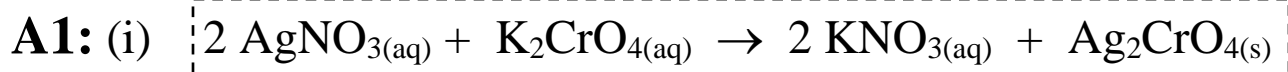
- A precipitation reaction can be written in its net ionic form.



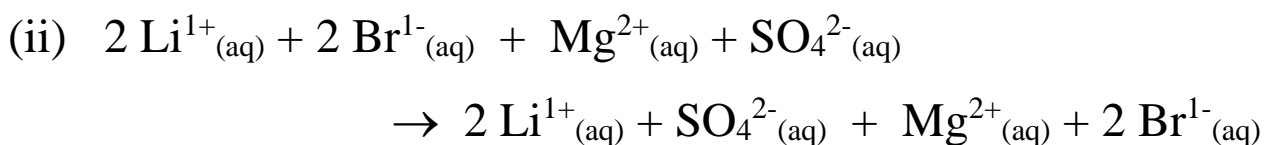
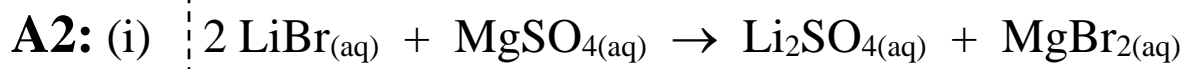
- By **learning the basic rules of solubility**, one can predict whether or not an ionic solid will significantly dissolve in water.

Ions that form Soluble Compounds	Exceptions	Ions that form Insoluble Compounds	Exceptions
Group-1 cations & NH_4^{1+}		CO_3^{2-}	Group-1 cations & NH_4^{1+}
NO_3^{1-}		CrO_4^{2-}	Group-1 cations & NH_4^{1+} , & Mg^{2+} , Ca^{2+}
$\text{C}_2\text{H}_3\text{O}_2^{1-}$ ($\text{CH}_3\text{COO}^{1-}$)		PO_4^{3-}	Group-1 cations & NH_4^{1+}
HCO_3^{1-}		S^{2-}	Group-1 cations & NH_4^{1+}
ClO_3^{1-}			
ClO_4^{1-}			
Cl^{1-} , Br^{1-} , I^{1-}	Ag^{1+} , Pb^{2+} , Hg_2^{2+}		Group-1 cations & NH_4^{1+} , & Sr^{2+} , Ba^{2+} . <i>Ca^{2+} is slightly soluble.</i>
SO_4^{2-}	Ag^{1+} , Pb^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+}		

Q1: Write (i) the molecular equation and (ii) the net ionic equation for the precipitation reaction that occurs between aqueous solutions of silver nitrate and potassium chromate.



Q2: Write (i) the molecular equation and (ii) the net ionic equation for the precipitation reaction that occurs between aqueous solutions of lithium bromide and magnesium sulfate.



no net ionic reaction occurs!

IN FACT NO CHEMICAL REACTION OCCURS!

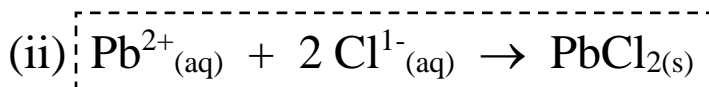
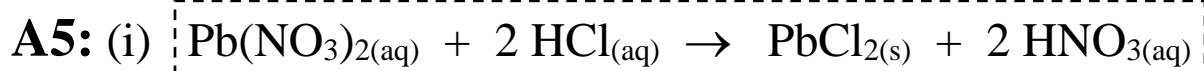
Q3: If a mixture containing 0.010 M Na^{1+} ions, 0.010 M Pb^{2+} ions, and 0.010 M Ag^{1+} ions, is treated dropwise with 1.00 M HCl, in what order will the ions precipitate?

A3: Ag^{1+} ions ($K_{\text{sp}} \text{AgCl} = 1.8 \times 10^{-10}$) and then Pb^{2+} ions ($K_{\text{sp}} \text{PbCl}_2 = 1.7 \times 10^{-5}$). The Na^{1+} ions would probably not precipitate.

Q4: How could a mixture of K^{1+} ions and Ca^{2+} ions be separated?

A4: Add dilute sulfuric acid to precipitate the Ca^{2+} ions. Then filter the mixture to capture the solid CaSO_4 .

Q5: 100.0 mL of 0.100 M lead (II) nitrate is added to 50.0 mL of 0.150 M HCl. (i) Write the balanced molecular equation for the reaction. (i) Write the net ionic equation for the reaction. (iii) Determine the limiting reagent. (iv) How many grams of precipitate are formed if there is 100% yield? (v) How many moles of the non-limiting reagent remain dissolved in the final mixture? (vi) Calculate the molar concentration for each of the aqueous ions present in the final mixture (*assume volumes are additive*).



(iii) $0.100 \frac{\text{mol}}{\text{L}} \text{Pb}(\text{NO}_3)_2 \times 0.1000 \text{L} = 0.0100 \text{mol} \div 1 \text{mol} = 0.0100$

$$\boxed{\begin{array}{l} \text{M} = \\ \frac{\text{Mol}}{\text{L}} \end{array}}$$

$0.150 \frac{\text{mol}}{\text{L}} \text{HCl} \times 0.0500 \text{L} = 0.0075 \text{mol} \div 2 \text{mol} = 0.0038$

(vi) $0.150 \frac{\text{mol}}{\text{L}} \text{HCl} \times 0.0500 \text{L} \times \frac{1 \text{ mol PbCl}_2}{2 \text{ mol HCl}} \times \frac{278.2 \text{ g}}{1 \text{ mol PbCl}_2} =$

1.04 g PbCl_2

(v) $0.0100 \text{ mol Pb}(\text{NO}_3)_2 \text{ initial} - 0.0038 \text{ mol Pb}(\text{NO}_3)_2 \text{ reacted} =$

$0.0062 \text{ mol Pb}(\text{NO}_3)_2 \text{ left}$

(vi) $0.0062 \text{ mol Pb}(\text{NO}_3)_2 \times 1 \rightarrow \frac{0.0062 \text{ mol Pb}^{2+}}{0.1500 \text{ L}} = 0.041 \text{ M Pb}^{2+}$

$0.0100 \text{ mol Pb}(\text{NO}_3)_2 \times 2 \rightarrow \frac{0.0200 \text{ mol NO}_3^{1-}}{0.1500 \text{ L}} = 0.133 \text{ M NO}_3^{1-}$

$0.0075 \text{ mol HCl} \times 1 \rightarrow \frac{0.0075 \text{ mol H}^{1+}}{0.1500 \text{ L}} = 0.050 \text{ M H}^{1+}$

- An electrolyte's **ion product** (Q_{sp}) is the instantaneous product of the electrolyte's cation and anion concentrations in the solution.

$$Q_{sp} = [\text{cation}]^X[\text{anion}]^Y$$

- If $Q_{sp} < K_{sp}$, then the solution is unsaturated (not at equilibrium) and no precipitate forms.
- If $Q_{sp} = K_{sp}$, then the solution is just saturated (at equilibrium) and is at the point of precipitation.
- If $Q_{sp} > K_{sp}$, then the solution is supersaturated (beyond equilibrium) and precipitate forms until $P = K_{sp}$.

Q6: Will a precipitate form if a solution mixture suddenly contains $[\text{Pb}^{2+}] = 0.075 \text{ M}$ and $[\text{Cl}^{1-}] = 0.025 \text{ M}$. ($K_{sp} = 1.7 \times 10^{-5}$)



$$Q_{sp} = [\text{Pb}^{2+}][\text{Cl}^{1-}]^2$$

$$Q_{sp} = [0.075][0.025]^2 = 4.7 \times 10^{-5} \text{ M}$$

$Q_{sp} > K_{sp} \dots$ yes, precipitate forms! $\text{Pb}^{2+}_{(aq)} + 2 \text{Cl}^{1-}_{(aq)} \rightarrow \text{PbCl}_{2(s)}$

Q7: A student mixes 250 mL of 0.060 M $\text{Pb}(\text{NO}_3)_2$ with 250 mL of 0.040 M HCl. Will a precipitate form? ($K_{sp} = 1.7 \times 10^{-5}$)



$$Q_{sp} = [\text{Pb}^{2+}][\text{Cl}^{1-}]^2$$

Be careful! When mixing solutions the volume changes and thus the ion concentrations change as well!

$[\text{Pb}^{2+}]$ goes from 0.060 M to 0.030 M because volume doubles!

$[\text{Cl}^{1-}]$ goes from 0.040 M to 0.020 M because volume doubles!

$$Q_{sp} = [0.030][0.020]^2 = 1.2 \times 10^{-5} \text{ M}$$

$Q_{sp} < K_{sp} \dots$ no precipitate forms!

Q8: If a mixture containing 0.010 M F^{1-} ions, 0.010 M SO_4^{2-} ions, and 0.010 M NO_3^{1-} ions, is treated dropwise with 1.00 M CaCl_2 , in what order will the ions begin precipitate? ($K_{\text{sp}} \text{CaF}_2 = 3.9 \times 10^{-11}$ and $K_{\text{sp}} \text{CaSO}_4 = 2.4 \times 10^{-5}$)

A8: F^{1-} ions will precipitate first and then SO_4^{2-} ions will precipitate. The NO_3^{1-} ions would probably not precipitate.

Q9: Will a precipitate form if a solution mixture suddenly contains $[\text{Ca}^{2+}] = 0.00040 \text{ M}$ and $[\text{F}^{1-}] = 0.00025 \text{ M}$. ($K_{\text{sp}} \text{CaF}_2 = 3.9 \times 10^{-11}$)

A9: $\text{CaF}_{2(\text{s})} \rightleftharpoons \text{Ca}^{2+}_{(\text{aq})} + 2 \text{F}^{1-}_{(\text{aq})}$

$$Q_{\text{sp}} = [\text{Ca}^{2+}][\text{F}^{1-}]^2$$

$$Q_{\text{sp}} = [0.00040][0.00025]^2 = 2.4 \times 10^{-11} \text{ M}$$

$Q_{\text{sp}} < K_{\text{sp}} \dots$ no, a precipitate will not form!

Q10: A student mixes 250 mL of 0.010 M $\text{Ca}(\text{NO}_3)_2$ with 250 mL of 0.010 M H_2SO_4 . Will a precipitate form? ($K_{\text{sp}} \text{CaSO}_4 = 2.4 \times 10^{-5}$)
Assume that the volumes are additive.

A10: $\text{CaSO}_{4(\text{s})} \rightleftharpoons \text{Ca}^{2+}_{(\text{aq})} + \text{SO}_4^{2-}_{(\text{aq})}$

$$Q_{\text{sp}} = [\text{Ca}^{2+}][\text{SO}_4^{2-}]$$

$[\text{Ca}^{2+}]$ goes from 0.010 M to 0.0050 M because volume doubles!

$[\text{SO}_4^{2-}]$ goes from 0.010 M to 0.0050 M because volume doubles!

$$Q_{\text{sp}} = [0.0050][0.0050] = 2.5 \times 10^{-5} \text{ M}$$

$Q_{\text{sp}} > K_{\text{sp}} \dots$ yes, a precipitate does form!

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Lesson-8

V – Acid-Base Titrations

A) Acid-Base Indicators

- Acid-base titration is a laboratory process in which equivalent quantities of acid and base are reacted.
- **The equivalence point** occurs when moles of H^{1+} = moles of OH^{1-}
- In an acid-base titration, an indicator is used to signal the end of the reaction (*this is how you know when to stop adding reagent*).
- **The end point** occurs when the acid-base indicator changes color.
- The choice of acid-base indicator is determined by the type of titration (reaction) being performed.

<i>Type of Reaction</i>	<i>pH at Equivalence Point</i>	<i>Appropriate Acid-Base Indicator</i>	<i>Color Change and pH Range of Color Change</i>
strong acid - weak base	Below 7	methyl orange	red to orange (3.1-4.4)
		bromcresol green	yellow to blue (3.8-5.4)
strong acid - strong base	Equal to 7	bromthymol blue	yellow to blue (6.0-7.6)
		litmus	red to blue (4.5-8.3)
weak acid - strong base	Above 7	phenolphthalein	colorless to pink (8-9)
		thymol blue	yellow to blue (8.0-9.6)

- Acid-base indicators are weak acids whose pK_a values are within the pH range of color change.



Q1: Predict the pH of a solution if a sample turns bromcresol green blue and bromthymol blue yellow.

A1: The pH of the solution is between 5.4 and 6.0.

Q2: Predict the pH of a solution if a sample turns bromthymol blue blue and thymol blue yellow.

A2: The pH of the solution is between 7.6 and 8.0.

B) Acid-Base Titration Problems

Q3: How many milliliters of 0.50 M H₂SO₄ would be needed to titrate 8.0 mL of 0.75 M NH₃?

- (i) Choose an appropriate indicator for this titration.
- (ii) How many milliliters of acid are required for neutralization?

A3: (i) Methyl orange or bromcresol green



$$0.0080 \text{ L} \times \frac{0.75 \text{ mol NH}_3}{1 \text{ L}} \times \frac{1 \text{ mol H}_2\text{SO}_4}{2 \text{ mol NH}_3} = 0.0030 \text{ mol H}_2\text{SO}_4$$

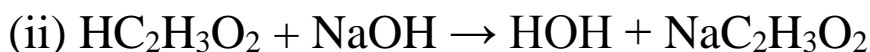
$$M = \frac{\text{mol}}{\text{L}}$$

$$0.50 \text{ M H}_2\text{SO}_4 = \frac{0.0030 \text{ mol H}_2\text{SO}_4}{X}$$

$$X = 6.0 \text{ mL H}_2\text{SO}_4$$

Q4: It takes 25.0 mL of 0.018 M HC₂H₃O₂ to neutralize 9.0 mL of NaOH. (i) Choose an appropriate indicator for this titration.
(ii) What is the molar concentration of the NaOH?

A4: (i) Thymol blue or phenolphthalein



$$0.0250 \text{ L} \times \frac{0.018 \text{ mol HC}_2\text{H}_3\text{O}_2}{1 \text{ L}} \times \frac{1 \text{ mol NaOH}}{1 \text{ mol HC}_2\text{H}_3\text{O}_2} \times \frac{1}{0.0090 \text{ L}} =$$

$$X = 0.050 \text{ M NaOH}$$

- The titration equation: $\rho_a M_a V_a = \rho_b M_b V_b$
 - ρ_a equals the number of ionizable H^{1+} ions from the acid
 - M_a equals the molarity of the acid
 - V_a equals the volume of the acid used in the titration
 - ρ_b equals the number of OH^{1-} ions from the base
 - M_b equals the molarity of the base
 - V_b equals the volume of the base used in the titration

Q5: It takes 30.0 mL of 0.024 M NH_3 to neutralize 18.0 mL H_2SO_4 .

- Choose an appropriate indicator for this titration.
- What is the molar concentration of the?

A5: (i) Methyl orange or bromocresol green

(ii) $\rho_a \underline{M_a} V_a = \rho_b M_b V_b$

$$(2)(X)(18.0) = (1)(0.024)(30.0)$$

$$\boxed{X = 0.020 \text{ M } H_2SO_4}$$

Q6: It takes 26.2 mL of 0.120 M HCl to neutralize 20.0 mL $Ba(OH)_2$.

- Choose an appropriate indicator for this titration.
- What is the molar concentration of the $Ba(OH)_2$?

A6: (i) Bromthymol blue or litmus

(ii) $\rho_a M_a V_a = \rho_b \underline{M_b} V_b$

$$(1)(0.120)(26.2) = (2)(X)(20.0)$$

$$\boxed{X = 0.0786 \text{ M } Ba(OH)_2}$$

Q7: It takes 15.0 mL of 0.040 M $HCHO_2$ to neutralize 0.050 M KOH .

- Choose an appropriate indicator for this titration.
- How many milliliters of KOH are needed for neutralization?

A7: (i) Thymol blue or phenolphthalein

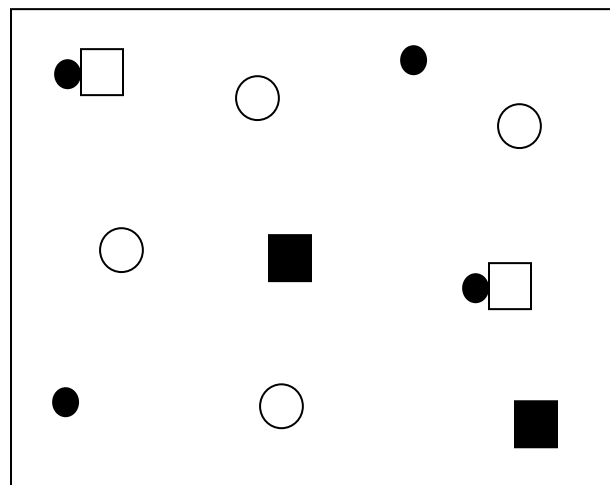
(ii) $\rho_a M_a V_a = \rho_b M_b \underline{V_b}$

$$(1)(0.040)(15.0) = (1)(0.050)(X)$$

$$\boxed{X = 12.0 \text{ mL } KOH}$$

Q8: If $\bullet\bigcirc$ represents HCl and if \blacksquare represent NaOH, then draw a particulate representation of the system halfway to neutralization if 1 M NaOH were being added to 1 M HCl. Label each particle in your drawing including any charge it may have. [Assume the diagram has 4 $\bullet\bigcirc$ before the titration began.]

A8:



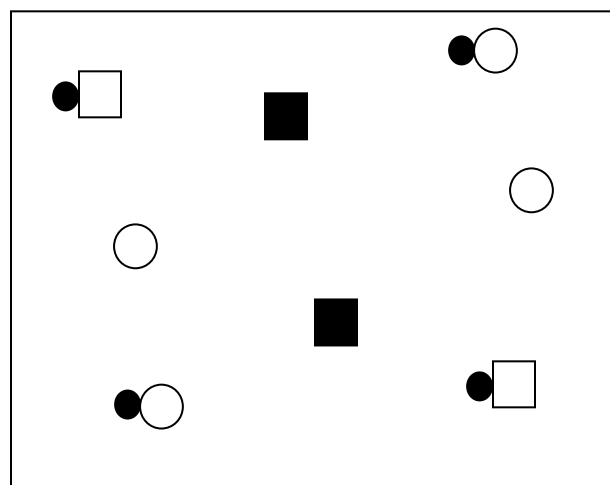
$\bullet\blacksquare$ is H_2O formed

\blacksquare is Na^{1+}

\bigcirc is Cl^{1-}

\bullet is H^{1+}

Q9: If the particulate representation below shows an acid-base system halfway to neutralization, then which of the following 1.0 M acids (HNO_3 or $\text{HC}_2\text{H}_3\text{O}_2$) was the one that was being neutralized by adding 1.0 M KOH? Explain.



$\bullet\blacksquare$ is H_2O formed

\blacksquare is K^{1+}

\square is OH^{1-}

\bullet is H^{1+}

$\bullet\bigcirc$ is unknown acid

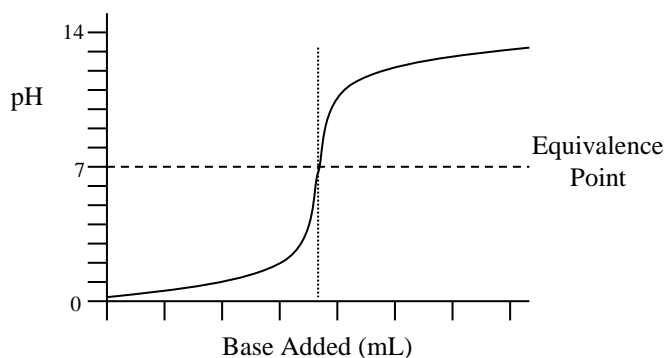
A9: $\text{HC}_2\text{H}_3\text{O}_2$ is the unknown acid. (1) $\bullet\bigcirc$ must be a weak acid since it is in its molecular form. $\text{HC}_2\text{H}_3\text{O}_2$ is a weak acid and HNO_3 is a strong acid. (2) Halfway to neutralization, $[\bullet\bigcirc]\text{-acid}$ equals $[\bigcirc]\text{-acid anion}$ which should be the case for a weak acid.

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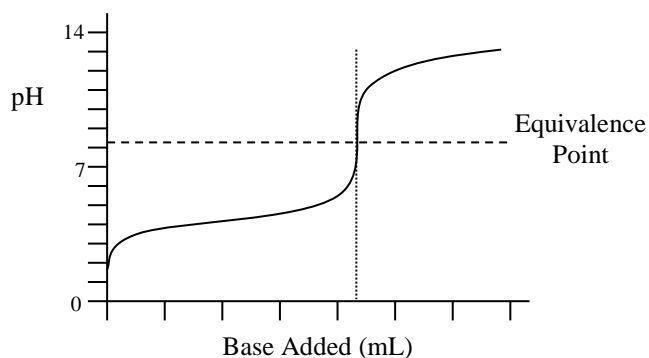
Lesson-9

VI – Plotting an Acid-Base Titration Curve

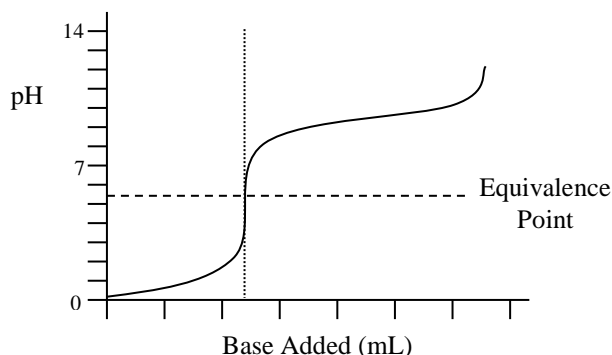
- The profile of a titration curve can tell you a lot about the acid and base in the titration.
- Strong acid-strong base curves have no horizontal inflection points in either the lower or upper portion of the curve.
- Weak acid-strong base curves have a horizontal inflection point in the lower portion of the curve.
- Strong acid-weak base curves have a horizontal inflection point in the upper portion of the curve.
- The equivalence point occurs at the vertical inflection point on the curve.
- Polyprotic acids have two equivalence points on the curve.



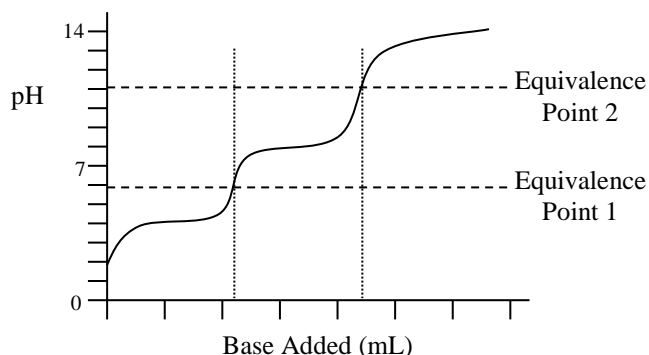
Adding a Strong Base to a Strong Acid



Adding a Strong Base to a Weak Acid



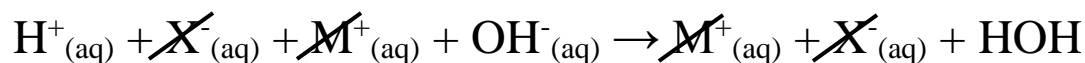
Adding a Weak Base to a Strong Acid



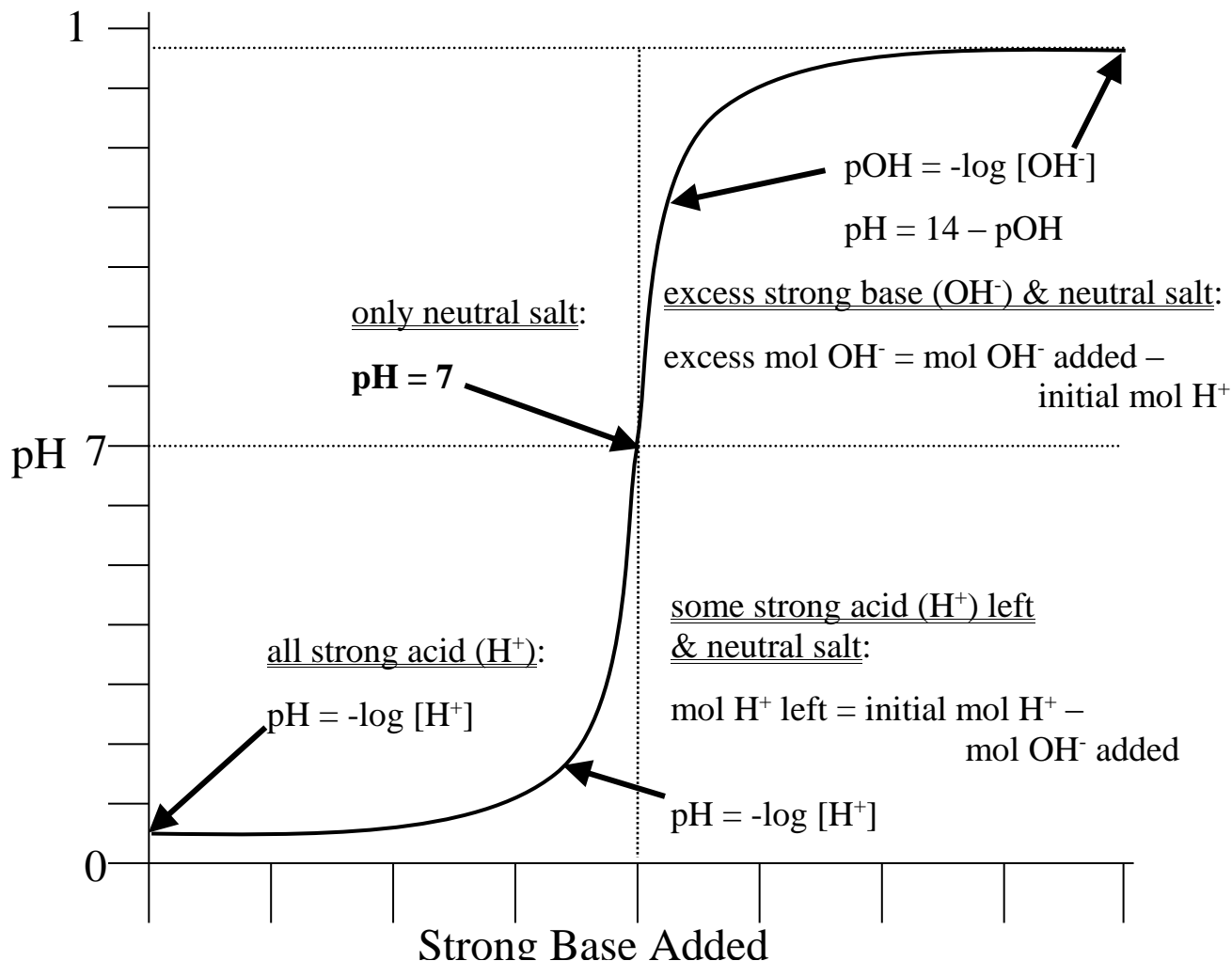
Adding Strong Base to a weak Polyprotic Acid

A) Plotting Titrations: Strong Acid with Strong Base

- Strong Acid (HX) + Strong Base (MOH) → Neutral Salt + Water



- Neutral salts do NOT react with water and thus do NOT change the pH of the water.



- It takes 5 points to plot this type of titration:

- (1) 0 mL of titrant added
- (2) 1 mL before neutralization
- (3) mL needed for neutralization
- (4) 1 mL after neutralization
- (5) double mL after neutralization

- Getting started:

☛ Calculate mL needed for neutralization: $\rho_a \mathbf{M}_a \mathbf{V}_a = \rho_b \mathbf{M}_b \mathbf{V}_b$

☛ Calculate initial moles of H¹⁺ to be titrated: $\rho_a \mathbf{M}_a \mathbf{V}_a$

Q1: Plot a titration curve for the neutralization of 15.00 mL of a 0.0200 M HCl solution with 0.0150 M NaOH solution.

A1: ☛ $\rho_a M_a V_a = \rho_b M_b V_b$

$$(1)(0.0200)(15.00) = (1)(0.0150)(X)$$

$$X = \underline{20.0 \text{ mL NaOH needed for neutralization}}$$

☛ Initial mol H^{1+}

$$\rho_a M_a V_a = (1)(0.0200\text{M})(0.01500\text{L}) = \underline{0.000300 \text{ mol H}^{1+}}$$

(1) at 0.0 mL NaOH added (initial)

$$\text{pH} = -\log[\text{HCl}] = -\log[0.0200] = \underline{1.699}$$

(2) at 19.0 mL NaOH added (before neutralization) tot. vol. = 34.0 mL

$$\text{mol OH}^{1-}_{\text{added}} = (0.0190\text{L})(0.0150\text{M}) = 0.000285 \text{ mol OH}^{1-}$$

$$\text{mol H}^{1+}_{\text{left}} = 0.000300 - 0.000285 = 0.000015 \text{ mol H}^{1+}_{\text{left}}$$

$$[\text{H}^{1+}_{\text{left}}] = 0.000015 \text{ mol H}^{1+} \div 0.0340\text{L} = 0.000441 \text{ M H}^{1+}_{\text{left}}$$

$$\text{pH} = -\log[\text{H}^{1+}_{\text{left}}] = -\log[0.000441] = \underline{3.356}$$

(3) at 20.0 mL NaOH added (at neutralization) pH = **7.000**

(4) at 21.0 mL NaOH added (after neutralization) tot. vol. = 36.0 mL

$$\text{mol OH}^{1-}_{\text{excess}} = (0.0010\text{L})(0.0150\text{M}) = 0.000015 \text{ mol OH}^{1-}$$

$$[\text{OH}^{1-}_{\text{excess}}] = 0.000015 \text{ mol OH}^{1-} \div 0.0360\text{L} = 4.17 \times 10^{-4} \text{ M}$$

$$\text{pOH} = -\log[\text{OH}^{1-}_{\text{excess}}] = -\log[4.17 \times 10^{-4}] = 3.38$$

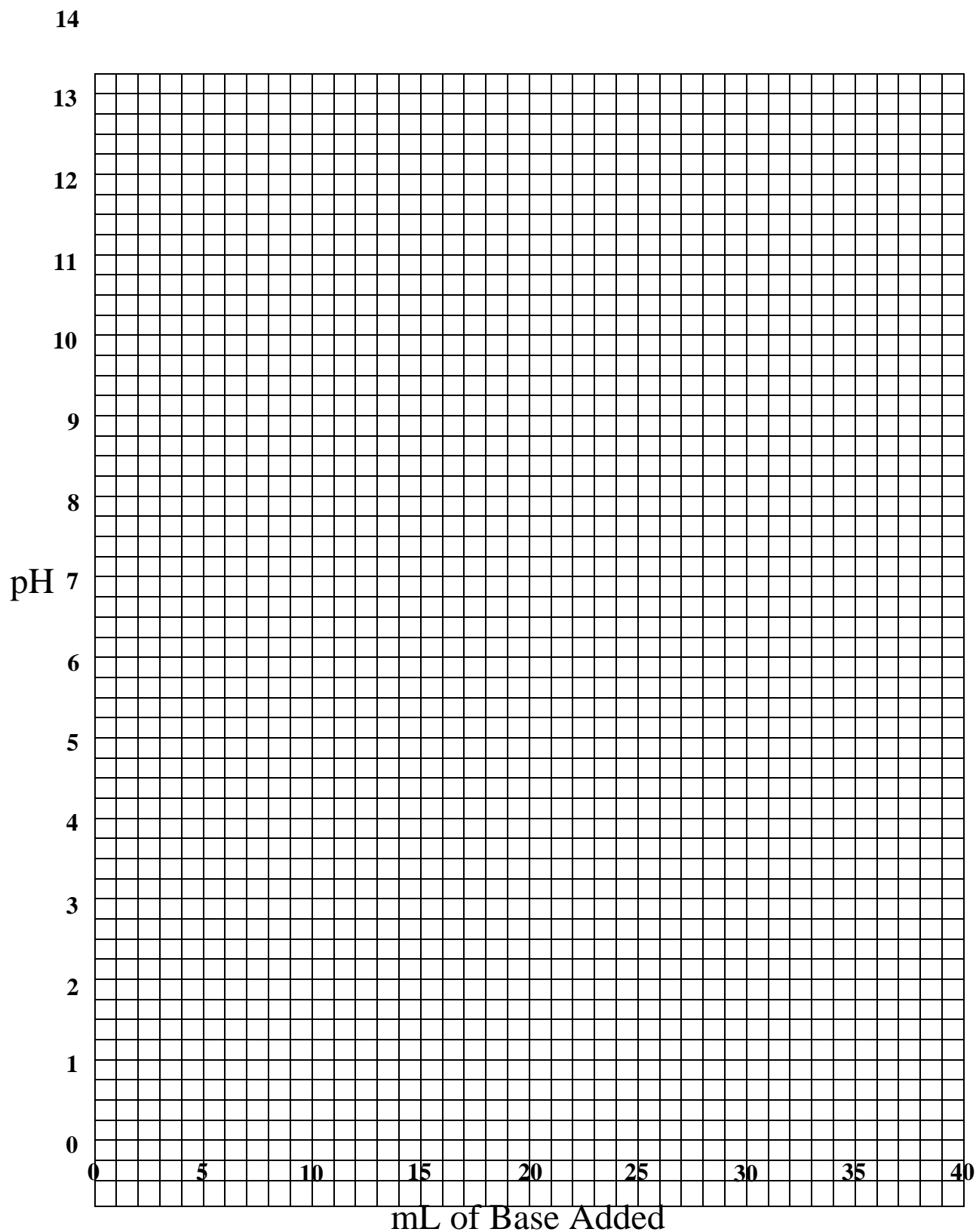
$$\text{pH} = \underline{10.62}$$

(5) at 40.0 mL NaOH added (after neutralization) tot. vol. = 55.0 mL

$$\text{mol OH}^{1-}_{\text{excess}} = (0.0200\text{L})(0.0150\text{M}) = 0.000300 \text{ mol OH}^{1-}$$

$$[\text{OH}^{1-}_{\text{excess}}] = 0.000300 \text{ mol OH}^{1-} \div 0.0550\text{L} = 0.00545 \text{ M}$$

$$\text{pOH} = -\log[\text{OH}^{1-}_{\text{excess}}] = -\log[0.00545] = 2.264 \rightarrow \text{pH} = \underline{\underline{11.736}}$$

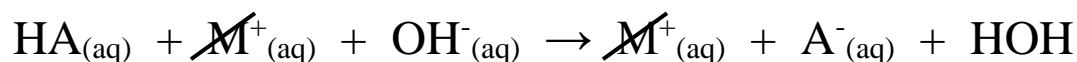


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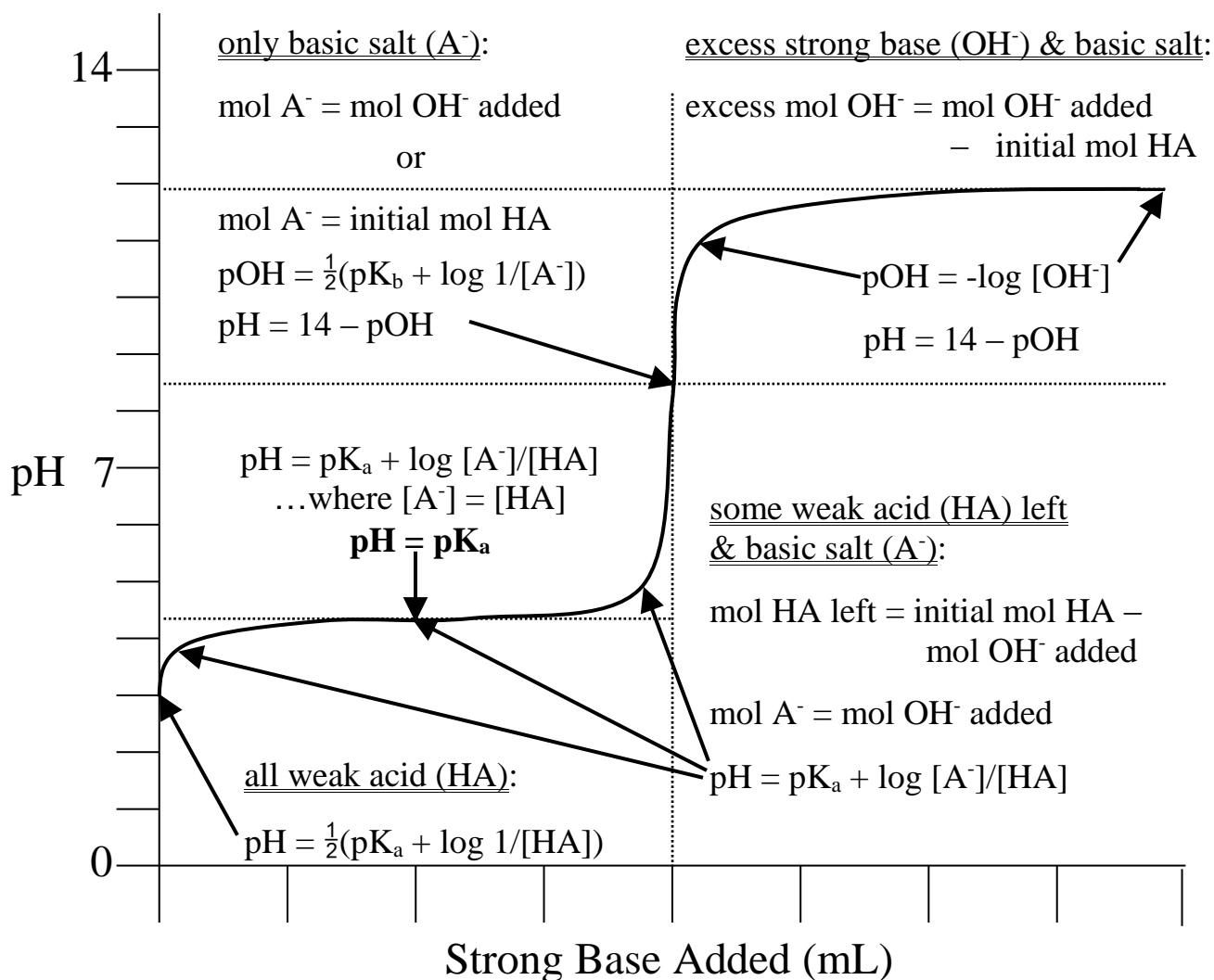
Lesson-10

B) Plotting Titrations: Weak Acid with a Strong Base

- Weak Acid (HA) + Strong Base (MOH) → Basic Salt + Water



- Basic salts DO react with water and thus DO change the pH of the water. Basic salts RAISE the pH of the water.



- It takes 7 points to plot this type of titration:
 - (1) 0 mL of titrant added
 - (2) 1 mL of titrant added
 - (3) half mL needed for neutralization
 - (4) 1 mL before neutralization
 - (5) mL needed for neutralization
 - (6) 1 mL after neutralization
 - (7) double mL for neutralization
- Getting started:
 - ☛ Calculate mL needed for neutralization: $\rho_a M_a V_a = \rho_b M_b V_b$
 - ☛ Calculate initial moles of weak acid (HA) to be titrated.
 $\text{moles of H}^+_{\text{initial}} = \rho_a M_a V_a$
 - ☛ Calculate pK_a of weak acid.
 $pK_a = -\log K_a$
 - ☛ Calculate pK_b of conjugate base of weak acid.
 $pK_b = 14 - pK_a$

Q1: Plot a titration curve for the neutralization of 15.00 mL of 2.00 M HF ($K_a = 6.8 \times 10^{-4}$) with 1.50 M NaOH.

A1: ☛ $\rho_a M_a V_a = \rho_b M_b V_b$
 $(1)(2.00)(15.00) = (1)(1.50)(X)$
 $X = \underline{20.0 \text{ mL NaOH needed for neutralization}}$

- ☛ Initial total mol H^{1+}
 $\rho_a M_a V_a = (1)(2.00M)(0.01500L) = \underline{0.0300 \text{ mol H}^{1+}}$
- ☛ $pK_a = -\log[K_a] =$
 $pK_a = -\log[6.8 \times 10^{-4}] = \underline{3.17 \text{ for HF}}$
- ☛ $pK_b = 14 - pK_a = 14 - 3.17 = \underline{10.83 \text{ for F}^{1-}}$

(1) at 0.0 mL NaOH added (initial)

$$\text{pH} = \frac{1}{2}[\text{pK}_a + \log(1/[\text{HF}])] = \frac{1}{2}[3.17 + \log(1/[2.00])] = \underline{\underline{1.43}}$$

(2) at 1.0 mL NaOH added (before neutralization)

$$\text{mol OH}^{1-}_{\text{added}} = (0.0010\text{L})(1.50\text{M}) = 0.0015 \text{ mol OH}^{1-}_{\text{added}}$$

$$\text{mol HF}_{\text{left}} = 0.0300 - 0.0015 = 0.0285 \text{ mol HF}_{\text{left}}$$

$$\text{pH} = \text{pK}_a + \log[\text{F}^{1-}]/[\text{HF}] = 3.17 + \log[0.0015^*]/[0.0285^*]$$

$$\text{pH} = \underline{\underline{1.89}}$$

(3) at 10.0 mL NaOH added ($\frac{1}{2}$ before neutralization)

$$\text{pH} = \text{pK}_a = \underline{\underline{3.17}}$$

(4) at 19.0 mL NaOH added (before neutralization)

$$\text{mol OH}^{1-}_{\text{added}} = (0.0190\text{L})(1.50\text{M}) = 0.0285 \text{ mol OH}^{1-}_{\text{added}}$$

$$\text{mol HF}_{\text{left}} = 0.0300 - 0.0285 = 0.0015 \text{ mol HF}_{\text{left}}$$

$$\text{pH} = \text{pK}_a + \log[\text{F}^{1-}]/[\text{HF}] = 3.17 + \log[0.0285^*]/[0.0015^*]$$

$$\text{pH} = \underline{\underline{4.45}}$$

(5) at 20.0 mL NaOH added (at neutralization) tot. vol. = 35.0 mL

at neutralization “all” mol HF is now equal to mol F¹⁻.

$$[\text{F}^{1-}] = [0.0300\text{mol} \div 0.0350\text{L}] = 0.857\text{M}$$

$$\text{pOH} = \frac{1}{2}[\text{pK}_b + \log(1/[\text{F}^{1-}])] = \frac{1}{2}(10.83 + \log[1/0.857]) = 5.45$$

$$\text{pH} = 14 - \text{pOH} = 14 - 5.45 = \underline{\underline{8.55}}$$

(6) at 21.0 mL NaOH added (after neutralization) tot. vol. = 36.0 mL

$$\text{mol excess OH}^{1-} = (0.0010\text{L})(1.50\text{M}) = 0.0015 \text{ mol OH}^{1-}_{\text{excess}}$$

$$[\text{OH}^{1-}_{\text{excess}}] = 0.0015\text{mol} \div 0.0360\text{L} = 0.042 \text{ M OH}^{1-}_{\text{excess}}$$

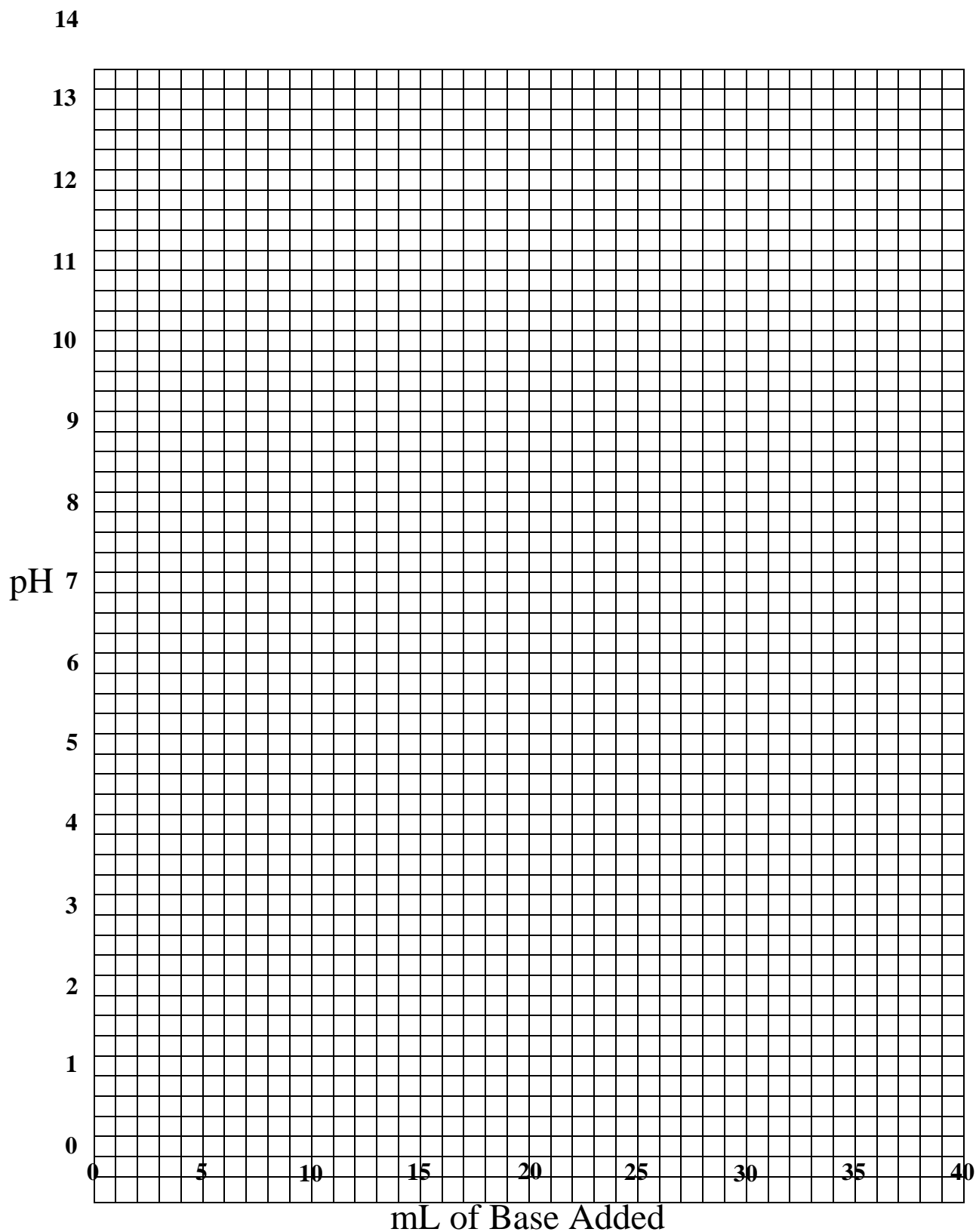
$$\text{pOH} = -\log[\text{OH}^{1-}_{\text{excess}}] = -\log[0.042 \text{ M}] = 1.38 \rightarrow \text{pH} = \underline{\underline{12.62}}$$

(7) at 40.0 mL NaOH added (after neutralization) tot. vol. = 55.0 mL

$$\text{mol excess OH}^{1-} = (0.0200\text{L})(1.50\text{M}) = 0.0300 \text{ mol OH}^{1-}_{\text{excess}}$$

$$[\text{OH}^{1-}_{\text{excess}}] = 0.0300\text{mol} \div 0.0550\text{L} = 0.545 \text{ M OH}^{1-}_{\text{excess}}$$

$$\text{pOH} = -\log[\text{OH}^{1-}_{\text{excess}}] = -\log[0.545 \text{ M}] = 0.264 \rightarrow \text{pH} = \underline{\underline{13.74}}$$

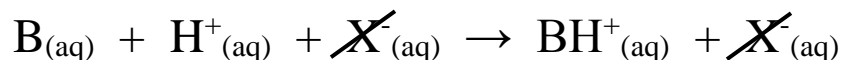


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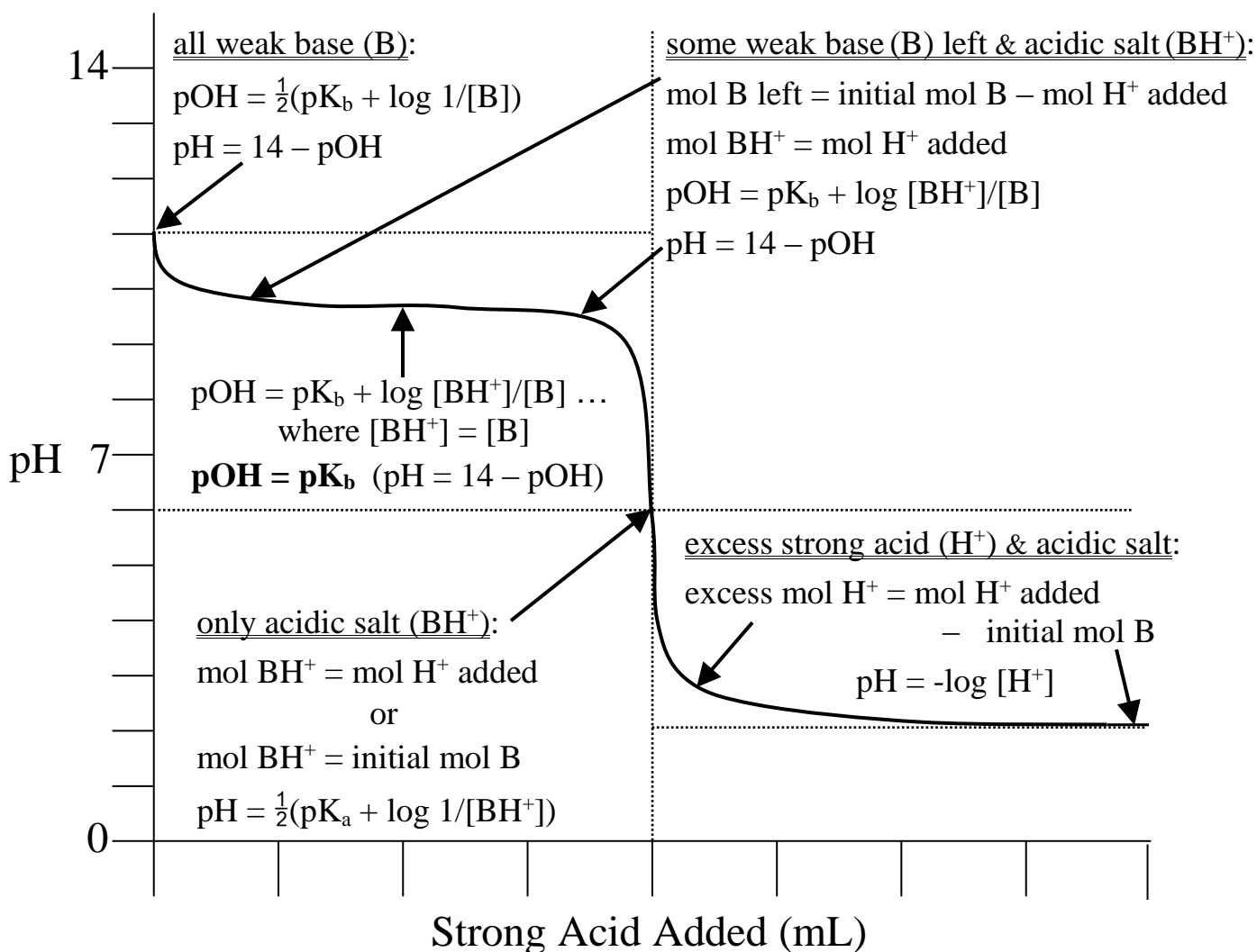
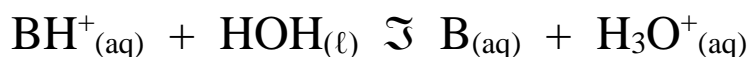
Lesson-11

C) Plotting Titrations: Weak Base with a Strong Acid

- Weak Base (B) + Strong Acid (HX) → Acidic Salt



- Acidic salts DO react with water and thus DO change the pH of the water. Acidic salts LOWER the pH of the water.



- It takes 7 points to plot this type of titration:
 - (1) 0 mL of titrant added
 - (2) 1 mL of titrant added
 - (3) half mL needed for neutralization
 - (4) 1 mL before neutralization
 - (5) mL needed for neutralization
 - (6) 1 mL after neutralization
 - (7) double mL for neutralization
- Getting started:
 - ☛ Calculate mL needed for neutralization: $\rho_a M_a V_a = \rho_b M_b V_b$
 - ☛ Calculate initial moles of weak base (B) to be titrated.
 $\text{moles of } B_{\text{initial}} = \rho_b M_b V_b$
 - ☛ Calculate pK_b of weak base (B).
 $pK_b = -\log K_b$
 - ☛ Calculate pK_a of conjugate acid of weak base.
 $pK_a = 14 - pK_b$

Q1: Plot a titration curve for the neutralization of 15.00 mL 0.200 M NH_3 ($K_b = 1.8 \times 10^{-5}$) with 0.150 M HCl.

A1: ☛ $\rho_a M_a V_a = \rho_b M_b V_b$
 $(1)(0.150)(X) = (1)(0.200)(15.00)$
 $X = \underline{20.0 \text{ mL HCl needed for neutralization}}$

☛ Initial tot. mol NH_3
 $\rho_b M_b V_b = (1)(0.200\text{M})(0.01500\text{L}) = \underline{0.00300 \text{ mol}}$

☛ $pK_b = -\log[K_b] = -\log[1.8 \times 10^{-5}]$
 $pK_b = -\log[1.8 \times 10^{-5}] = \underline{4.74}$

☛ $pK_a = \underline{9.26}$

(1) at 0.0 mL HCl added (initial)

$$\text{pOH} = \frac{1}{2}[\text{pK}_b + \log(1/[\text{NH}_3])]$$

$$\text{pOH} = \frac{1}{2}[4.74 + \log(1/[0.200])] = 2.72 \rightarrow \text{pH} = \underline{\underline{11.28}}$$

(2) at 1.0 mL HCl added (before neutralization)

$$\text{mol H}^{1+}_{\text{added}} = (0.0010\text{L})(0.150\text{M}) = 0.00015 \text{ mol H}^{1+}_{\text{added}}$$

$$\text{mol NH}_3_{\text{left}} = 0.00300 - 0.00015 = 0.00285 \text{ mol NH}_3_{\text{left}}$$

$$\text{mol NH}_4^{1+}_{\text{formed}} = \text{mol H}^{1+}_{\text{added}}$$

$$\text{pOH} = \text{pK}_b + \log[\text{NH}_4^{1+}]/[\text{NH}_3]$$

$$\text{pOH} = 4.74 + \log[0.00015]/[0.00285] = 3.46 \rightarrow \text{pH} = \underline{\underline{10.54}}$$

(3) at 10.0 mL HCl added (1/2 before neutralization)

$$\text{pOH} = \text{pK}_b = 4.74 \rightarrow \text{pH} = \underline{\underline{9.26}}$$

(4) at 19.0 mL HCl added (before neutralization)

$$\text{mol H}^{1+}_{\text{added}} = (0.0190\text{L})(0.150\text{M}) = 0.00285 \text{ mol H}^{1+}_{\text{added}}$$

$$\text{mol NH}_3_{\text{left}} = 0.00300 - 0.00285 = 0.00015 \text{ mol NH}_3_{\text{left}}$$

$$\text{pOH} = \text{pK}_b + \log[\text{NH}_4^{1+}]/[\text{NH}_3]$$

$$\text{pOH} = 4.74 + \log[0.00285]/[0.00015] = 6.02 \rightarrow \text{pH} = \underline{\underline{7.98}}$$

(5) at 20.0 mL HCl added (at neutralization) tot. vol. = 35.0 mL
at neutralization "all" mol NH₃ is now equal to mol NH₄¹⁺.

$$[\text{NH}_4^{1+}] = [0.00300\text{mol} \div 0.0350\text{L}] = 0.0857\text{M}$$

$$\text{pH} = \frac{1}{2}[\text{pK}_a + \log(1/[\text{NH}_4^{1+}])]$$

$$\text{pH} = \frac{1}{2}[9.26 + \log(1/[0.0857])] = \underline{\underline{5.16}}$$

(6) at 21.0 mL HCl added (after neutralization) tot. vol. = 36.0 mL

$$\text{mol excess H}^{1+} = (0.0010\text{L})(0.150\text{M}) = 0.00015 \text{ mol H}^{1+}_{\text{excess}}$$

$$[\text{H}^{1+}_{\text{excess}}] = 0.00015\text{mol} \div 0.0360\text{L} = 0.0042 \text{ M H}^{1+}_{\text{excess}}$$

$$\text{pH} = -\log[\text{H}^{1+}_{\text{excess}}] = -\log[0.0042 \text{ M}] = \underline{\underline{2.38}}$$

(7) at 40.0 mL HCl added (after neutralization) tot. vol. = 55.0 mL

$$\text{mol excess H}^{1+} = (0.0200\text{L})(0.150\text{M}) = 0.00300 \text{ mol H}^{1+}_{\text{excess}}$$

$$[\text{H}^{1+}_{\text{excess}}] = 0.00300\text{mol} \div 0.0550\text{L} = 0.0545 \text{ M H}^{1+}_{\text{excess}}$$

$$\text{pH} = -\log[\text{H}^{1+}_{\text{excess}}] = -\log[0.0545 \text{ M}] = \underline{\underline{1.26}}$$

